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THE PINACOL REDUCTION OF KETONES AT PLATED

COPPER GAUZE CATHODES

BY

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INTRODUCTION

Amalgams of active metals such as aluminum and magnesium have been the reducing agents used most for converting ketones to the corresponding pinacols. This technique suffers from serious disadvantages, however, such as the special preparations of the amalgam, use of large volumes of solvent, and the formation of large quantities of flocculent precipitates which interfere with the isolation of the product. Reduction of the ketone at the cathode of an electrolytic cell avoids these difficulties and is especially adapted for large scale operations. The principal problem that arises in the use of this technique is to obtain a cathode which will give high current efficiencies, i. e. produce little hydrogen.

The problem.- The electrodes used most have been made of the metal, cast or rolled into the proper shape, with or without a plating of another metal. It is, however, frequently inconvenient to make this type of electrode in the absence of metallurgical equipment and commercially available sheet metals frequently contain small amounts of impurities which interfere with the reduction. The purpose of this study was to develop a cathode material which was readily available, and would produce the desired

reduction in good yield with high current efficiency. The material selected was copper gauze. Besides its availability and purity, copper gauze has the additional advantages of being light, easily shaped into the desired form, and readily plated with other metals. Copper gauze, both plain and plated, has been used as an electrode in the reduction of various substances,^{1a,b} but no systematic study has been made of it as the cathode for the reduction of either ketones or any other class of compounds. The overvoltage of pure copper is too low to reduce the ketone by itself, but by plating the copper with a metal of high overvoltage, it has been found that the cathode behaves as if made of that material even though the plating is so thin as to be virtually invisible.

Method of study.- P-hydroxypropioophenone was selected as the ketone and its reduction was studied varying the cathode, pH, temperature, and current density. Besides being commercially available and relatively inexpensive, this compound has the advantage of being soluble in aqueous alkali and since it is an unsymmetrical ketone, it can form two isomeric pinacols so that the ratio of isomers formed under various conditions can also be studied.

Other workers have reported the electrolytic reduction of this ketone at a lead cathode,² but no detailed study has been made and the yields of pinacol have been low. The apparatus used was similar to that previously described.³ The metals selected for plating were ones which were expected

to have a high overvoltage so as to bring about the desired reaction. No really accurate method for determination of overvoltage has been developed, however, it is possible to make qualitative comparisons and on the basis of the work of Caspari⁴ and Tafel,⁵ lead, mercury, tin, cadmium, thallium, arsenic, antimony, and bismuth were selected. The results obtained are summarized in Table I. The yields reported are the total crude yield, containing a mixture of the dl and meso isomers after the separation of gummy materials and unreacted starting material. This was felt to give the best idea of actual yield obtained since separation of the isomers entailed some handling losses. The process was also too tedious to be practical for individual runs.

DISCUSSION

When using cathodes of 40 and 60 mesh, the current efficiency depended on the plating metal used. In the case of 20 mesh gauze and copper wire of 26 gauge the current efficiency was very low in all cases, even when plated with metals which gave high current efficiencies with the finer mesh. Since it was inconvenient to separate unreacted starting material, an excess of current was

generally passed through the cell. When the amount of current used was greatly in excess of that needed, for the formation of the pinacol in acid medium, no attack on the pinacol was noted. However, when an excess of current was used in alkaline medium there was further reduction of the pinacol giving rise to gummy products. Consequently, the amount of current used in alkaline medium was just slightly in excess of the theoretical.

Cathodes.- The metals used in plating the copper gauze and the coatings obtained were critical. It was noted that in the case of mercury, as little as 6 mg. of mercury over a surface area of 330 sq. cm. effected a reduction in acid medium, whereas, a heavily mercury plated cathode gave a smaller yield of pinacol. It was also noted that the cathode originally plated with 6 mg. of mercury could be used in two more such reactions before it was necessary to replate the cathode. When this replating was found necessary 1.5 mg. of mercury reproduced the original activity. In alkaline medium, the heavily mercury plated cathode was found most efficient. Most probably a sodium amalgam was formed, for when a pool of mercury was used as the cathode, excellent results were obtained, but the pool began to solidify and when washed with water, a steady evolution of hydrogen was noted. Copper gauze was also heavily plated with nickel and silver and these were then amalgamated. The results obtained were poorer than for amalgamated copper.

TABLE I

Run No.	Cathode	Catholyte	AmpereHours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density amps/cm ²
1.	Pb light on 40 mesh copper	85% H ₃ PO ₄	4.5 (250%)	15	25	0		0.0065
2.	Pb light on 40 mesh copper	170 ml methanol, 70 ml H ₂ O, 3 ml H ₃ PO ₄	3.3 (184%)	10-14	30	0		0.0048
3.	Pb heavy on 40 mesh copper	0.3 N NaOH	3.9 (220%)	10-14	25	9.0 gummy		0.0057
4.	Pb light on 40 mesh copper	180 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	3.9 (220%)	10	20	18.0	149-62	0.0057
5.	Pb heavy on 40 mesh copper	180 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	6.15 (265%)	10	20	10.0	150-65	0.0057
6.	Pb heavy on 40 mesh copper	180 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	5.1 (191%)	8	10	14.6	149-64	0.0305
7.	Pb light on 40 mesh copper	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	3.85 (202%)	8	10	44.0	147-59	0.0305
8.	Pb light on 40 mesh copper	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	5.35 (302%)	8	30	40.0	149-62	0.0305
9.	Pb light on 40 mesh copper	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	5.6 (316%)	8	50	21.0	161-73	0.0305

Run No.	Cathode	Catholyte	Ampere Hours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density amps/cm ²
10.	Pb light on 40 mesh copper (Reused # 9)	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	5.6 (316%)	8	25-40	43.0	160-170	0.0305
11.	Pb light on 40 mesh copper	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	4.25(300%)	8	40	41.0	140-52	0.0305
12.	Pb light on 40 mesh copper	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	4.9 (276%)	8	25	45.0	149-62	0.0305
13.	Pb light on 40 mesh copper	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	6.3 (350%)	10	25	41.5	167-73	0.0079
14.	Pb light on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 2 ml H ₂ SO ₄	2.2 (240%)	7.5	25	40.0	154-63	0.0063
15.	Pb light on 60 mesh copper (Reused #14)	125 ml methanol, 35 ml H ₂ O, 2 ml H ₂ SO ₄	2.2 (240%)	7.5	25	32.0	146-148 St. Mat.	0.0063
16.	Pb light on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	7.5	30	24.0	148-156	0.0063
17.	Pb light on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 1 ml H ₂ SO ₄	3.3 (360%)	7.5	30	0		0.0063
18.	Pb light on 60 mesh copper No Diaphragm.	125 ml methanol, 35 ml H ₂ O, 2 ml H ₂ SO ₄	3.3 (360%)	7-30	30	0		0.0063
19.	Pb light on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 5 ml H ₂ SO ₄	3.3 (360%)	15-30	30	16.0	144-47	0.0063

Run No.	Cathode	Catholyte	AmpereHours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density amps/cm ²
20.	Pb light on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 4 ml H ₂ SO ₄	2.75 (300%)	12-25	30	38.0	151-63	0.0063
21.	Pb light on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	12.5	25	50.0	147-58	0.0066
22.	Pb light on 60 mesh copper	160 ml methanol, 60 ml H ₂ O, 6 ml H ₂ SO ₄	2.16 (123%)	10	25	26.0	147-72	0.0061
23.	Pb light on 60 mesh copper	75 ml methanol, 30 ml H ₂ O, 15 ml HAC 6 g. NaAc	2.2 (175%)	20	30	0	0	0.0063
24.	Bi on 40 mesh from BiNO ₃	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	3.0 (166%)	10	25	50.0	155-65	0.0053
25.	Bi on 60 mesh from Bi O ₂ CO ₃	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	2.4 (134%)	7.5	25	21.0	163-73	0.0049
26.	Reused #25	200 ml methanol, 70 ml H ₂ O, 4 ml H ₂ SO ₄	2.75 (150%)	7.5	25	20.0	173-79	0.0049
27.	Bi on 60 mesh from Bi O ₂ CO ₃ Dipped in CuSO ₄	140 ml methanol, 45 ml H ₂ O, 2 ml H ₂ SO ₄	2.62 (300%)	7.5	25	18.0	144-54	0.0054
28.	Reused #27	140 ml methanol, 45 ml H ₂ O, 2 ml H ₂ SO ₄	2.62 (300%)	7.5	25	28.0	138-54	0.0054
29.	Reused #28	140 ml methanol, 45 ml H ₂ O, 2 ml H ₂ SO ₄	2.62 (300%)	7.5	25	28.0	140-50	0.0054

Run No.	Cathode	Catholyte	AmpereHours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density amps/cm ²
30.	As light on 60 mesh copper	125 ml methanol, 30 ml H ₂ O, 2 ml H ₂ SO ₄	2.2 (240%)	7.5	25	0		0.0057
31.	As heavy on 60 mesh copper	125 ml methanol, 30 ml H ₂ O, 2 ml H ₂ SO ₄	2.2 (240%)	7.5	25	0		0.0057
32.	Sn heavy on 60 mesh copper	125 ml methanol, 30 ml H ₂ O, 2 ml H ₂ SO ₄	2.2 (240%)	7.5	25	0		0.0057
33.	Sb heavy on 60 mesh copper	125 ml methanol, 30 ml H ₂ O, 2 ml H ₂ SO ₄	2.2 (240%)	7.5	25	0		0.0057
34.	Cd heavy on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.75(300%)	7.5	25	48.0	145-55	0.0051
35.	Reused #34	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	7.5	25	40.0	144-57	0.0051
36.	Tl light on 60 mesh copper	240 ml methanol, 70 ml H ₂ O, 6 ml H ₂ SO ₄	4.4 (240%)	10.0	25	23.0	156-68	0.0067
37.	Tl heavy on 60 mesh copper	240 ml methanol, 70 ml H ₂ O, 6 ml H ₂ SO ₄	4.4 (360%)	10.0	25	10.0	158-76	0.0067
38.	Hg light on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.75(300%)	15	30	36.0	144-53	0.006
39.	Hg heavy on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.75(300%)	15	30	30.0	154-71	0.006

Run No.	Cathode	Catholyte	AmpereHours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density amps/cm ²
40.	Hg light on 60 mesh copper	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.0 (240%)	15	25	50.0	141-49	0.006
41.	Hg from 8 mg. HgCl ₂ on 60 mesh	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.0 (240%)	15	25	46.0	150-58	0.0061
42.	Reused #41	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.0 (240%)	15	30	40.0	145-54	0.0061
43.	Reused #42	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.0 (240%)	15	25	0		0.0061
44.	Replated #43 with 1.5 mg. Hg.	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	3.3 (360%)	15	25	30.0	144-58	0.0061
45.	Hg from 12 mg. HgCl ₂ on 60 mesh	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	15	25	18.0	144-56	0.0063
46.	Hg from 8 mg. HgCl ₂ on 60 mesh	130 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	12.5	25	44.0	147-56	0.0067
47.	Hg heavy on 60 mesh copper	145 ml 85% H ₃ PO ₄	2.2 (240%)	12.5	95	0		0.0067
48.	Hg from 12 mg. HgCl ₂ on 60 mesh	125 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	12.5	25	46.0	149-61	0.0063
49.	Hg from 10 mg. HgCl ₂ on 60 mesh	140 ml ethanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	12.5	25	48.0	152-64	0.0067

Run No.	Cathode	Catholyte	Ampere Hours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density, amps/cm ²
50.	Hg-Ni on 60 mesh copper (10 mg.Hg)	135 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	12.5	25	36.0	140-54	0.0067
51.	Hg-Ni on 60 mesh copper (20 mg.Hg)	135 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	12.5	25	38.0	146-58	0.0067
52.	Hg-Ag on 60 mesh copper (50 mg.Hg)	135 ml methanol, 35 ml H ₂ O, 3 ml H ₂ SO ₄	2.2 (240%)	12.5	25	14.0	162-74	0.0067
53.	Hg heavy on 60 mesh copper	85 ml methanol, 40 ml H ₂ O, 15 ml H ₃ PO ₄	3.85 (310%)	17.5	15	31.5	140-80	0.0067
54.	Reused #53	80 ml methanol, 40 ml H ₂ O, 15 ml HAc 6 g., NaAc	2.75 (220%)	22.5	30	34.3	180-205	0.0067
55.	Hg heavy on 60 mesh copper	85 ml methanol, 40 ml H ₂ O, 3 ml H ₂ SO ₄	1.8 (145%)	10	20	22.9	154-193	0.0073
56.	Hg heavy on 60 mesh copper	75 ml methanol, 30 ml H ₂ O, 15 ml HAc 6 g., NaAc	2.2 (177%)	15	25	21.4	165-204	0.0067
57.	Hg heavy on 60 mesh copper	85 ml T-Butyl alc. 30 ml H ₂ O, 6 g NaAc 15 ml HAc	1.8 (140%)	30	35	12.8	150-64	0.0055
58.	Hg heavy on 60 mesh copper	35 ml T-Butyl alc. 45 ml methanol, 18 ml HAc, 6 g. NaAc 40 ml H ₂ O	2.0 (160%)	35	30	33.0	150-84	0.036

Run No.	Cathode	Catholyte	Ampere Hours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density, amps/cm ²
59.	Hg heavy on 60 mesh copper	160 ml methanol, 60 ml H ₂ O, 6 ml H ₂ SO ₄	2.2 (123%)	10	25	48.0	172-90	0.0067
60.	Hg light on 60 mesh copper (12 mg. Hg.)	160 ml methanol, 60 ml H ₂ O, 6 ml H ₂ SO ₄	2.2 (123%)	10	25	25.0	161-200	0.0058
61.	Hg heavy on 40 mesh copper	170 ml methanol, 60 ml H ₂ O, 6 ml H ₂ SO ₄	4.0 (227%)	10	25	38.0	150-87	0.0060
62.	Hg heavy on 20 mesh copper	170 ml methanol, 60 ml H ₂ O, 6 ml H ₂ SO ₄	4.0 (227%)	10	25	0		0.0077
63.	Hg heavy on 40 mesh copper	160 ml methanol, 60 ml H ₂ O, 6 ml H ₂ SO ₄	4.0 (227%)	10	25	44.0	151-74	0.0060
64.	Hg heavy on 40 mesh copper	160 ml methanol, 60 ml H ₂ O, 6 ml H ₂ SO ₄	4.0 (227%)	10	25	49.0	144-79	0.0060
65.	Hg heavy on 60 mesh copper	2 N NaOH	2.1 (100%)	12.5	30	35.0	173-79	0.0604
66.	Hg pool	2 N NaOH	2.1 (153%)	12.5	30	Acetylated & Dehydrated		0.1783
67.	Hg pool	2 N NaOH	2.1 (139%)	12.5	30	Schotten- Baumann		0.1783
68.	Hg heavy on 60 mesh copper	2 N NaOH	2.1 (200%)	12.5	30	44.0	150-88	0.0362

Run No.	Cathode	Catholyte	AmpereHours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density amps/cm ²
69.	Hg pool	2 N NaOH	2.1 (230%)	12.5	30	98.0	150-74	0.1783
70.	Hg heavy on 60 mesh copper	2 N NaOH	1.8 (100%)		25	50.0	150-60	0.00093
71.	Hg heavy on 60 mesh copper	2 N NaOH	2.1 (120%)	12.5	25	74.0	142-159	0.106
72.	Hg heavy on 60 mesh copper	2 N NaOH	2.65(150%)	12.5	25	12.0	186-200	0.106
73.	Hg-Na pool	2 N NaOH	2.1 (127%)	12.5	25	68.0	153-63	0.1684
74.	Hg-Na pool	2 N NaOH	2.5 (140%)	12.5	25	7.0	172-79	0.1684
75.	Hg heavy on 60 mesh copper	2 N NaOH	2.5 (140%)	7.5	30	63.0	150-65	0.0076
76.	Hg heavy on 60 mesh copper	2 N NaOH	2.5 (140%)	7.5	30	87.0	150-65	0.0076
77.	Hg heavy on 60 mesh copper	2 N NaOH	4.2 (310%)	7.5	15	90.0	150-165	0.2415
78.	Hg heavy on 60 mesh copper	5 N NaOH	2.8 (225%)	7.5	15	17.2	170-85	0.0073
79.	Hg heavy on 60 mesh copper	30% NaOH	2.75(220%)	10	30	26.0	146-71	0.0067
80.	Hg heavy on 60 mesh copper	2 N NaOH	1.65(100%)	7.5	20	95.0	155-70	0.007

Run No.	Cathode	Catholyte	Ampere Hours % of Theor.	Volts	Temp °C	% Crude Yield	M.P. °C	Current Density amps/cm ²
81.	Hg pool	2 N NaOH	1.93 (108%)	7.5	25	95.0	150-70	0.147
82.	Hg heavy on 60 mesh copper	2 N NaOH	2.0 (108%)	7.5	25	100.0	145-65	0.103
83.	Hg heavy on 60 mesh copper	2 N NaOH	1.93 (108%)	7.5	25	98.0	150-163	0.147
1.	Hg heavy on 60 mesh copper	10.0 g.p.-Methoxy- propionophenone 85 ml methanol, 30 ml H ₂ O, 13 ml HAC 5 g. NaAc	3.3 (185%)	15	25	26.0	179-90	0.0067

With lead plated cathodes, no definite minimum of lead concentration was established so that just light and heavy platings were used; a light plating being one where copper was visible. In order to obtain uniformly light plated electrodes, heavily plated ones were first prepared and then dipped in a solution of 3-5% copper sulfate. These dipped cathodes were reactive and fair reductions in acid medium were obtained. Heavily coated lead gave poorer results in acid medium and lead cathodes of either type gave very low current efficiencies in alkaline medium. Results with cadmium were quite similar to those of lead, while smaller yields were obtained with bismuth and thallium. The cathodes plated with arsenic, antimony, and tin did not produce the desired reaction.

Medium.- Next to the nature of the cathode, the factor most affecting the course of the reduction was the composition of the catholyte. The acid medium consisted of methanol and water as the solvent for the ketone and sulfuric acid as the electrolyte. The amount of sulfuric acid necessary was kept to a near minimum, but when only 1 ml. was used there was a sharp drop in current efficiency. Larger amounts than 5 ml. of sulfuric acid were not used as, at this point, a decrease in yield of pinacol was obtained although current efficiency remained high. Thus 3 ml. of concentrated sulfuric acid per 5 g. ketone was found to give the best results. Similar reactions using

phosphoric acid in place of the sulfuric acid gave low current efficiency, except when using heavily plated mercury cathodes. The use of syrupy phosphoric acid as the electrolyte and solvent was hindered by excessive foaming due to the low current efficiency and starting material was recovered. Ethanol and water was also used as the solvent, but without increasing the yield.

For Alkaline medium, 2 N sodium hydroxide was used as solvent and electrolyte. As the concentration of the sodium hydroxide was increased, the pinacol precipitated out, however, this was a disadvantage as the cathode became coated with product and thus reduction was hindered. This medium proved the most useful as it was easy to prepare, economical, and the product easily recovered and purified.

In addition to strongly acid and alkaline media, buffered solutions, with a pH of 5.6- 7, of acetic acid and sodium acetate were also used. These were characterized by only fair current efficiency with mercury cathodes and very low current efficiency with lead electrodes.

Temperature.- Lowering the temperature below 20° had no noticeable effect on the course of the reduction. Above 35-40° the yields dropped off in acid medium. No study was made of the effects of temperature on yield in alkaline medium, but all runs were made between 20-30°.

Current density.- High current density had little effect in either acid or alkaline medium on the total yield or proportion of the two isomers formed, however, if it was too low, no reduction occurred. Current density was regulated both by the amperage passed through the cell and the surface area of the cathode. By reducing the area of the cathode, a high current density could be obtained without high amperage so that overheating of the cell was avoided.

Purification of pinacol.- After separating the non-crystalline by-products and unreacted starting material, the crude product melted over a range of 10-15° from about 150-165°, with each run having a slightly different melting point. Since two isomeric pinacols can be formed from this reduction, it seemed likely that this product was a mixture. Attempts to effect a separation by recrystallizing from acetic acid were unsuccessful. With each recrystallization, there was a loss of 50% in material without a significant rise in melting point. Since it seemed possible that a pinacolone rearrangement occurred during the heating with acetic acid, acetone and acetone-iso-propyl ether were tried as solvents. Again there was extensive loss of material without appreciable improvement in the melting point. Chromatographic methods were also employed in attempts to effect a separation. Silica gel was used as the adsorbent, with ether-acetone as eluant. Again, no effective separation could be made

although there was a slight improvement in the melting point. During runs using 20% sodium hydroxide solution as electrolyte, it had been noted that the pinacol formed precipitated out. This insolubility in strong alkali was therefore tried as a basis for making a separation. If the crude product was dissolved in dilute sodium hydroxide and then enough solid sodium hydroxide added to make a 20% solution, no solid separated on cooling. However, it was found that cold 20% sodium hydroxide had a selective solvent action for one (isomer B) and that if the crude mixtures were extracted three times with 20% alkali, a fairly clean separation could be made, with little loss of product.

Isomer B separated on acidifying the alkaline solution to give a product melting at about 175-185°. The crude material gave approximately equal amounts of the two isomers. Purification of these isomers was difficult due to their tendency to occlude solvents and because they had little tendency to separate from each other on recrystallization. The purest sample of isomer A obtained melted at 204-208°. (204-206° lit.)⁶

Proof of structure.- Two isomers of this pinacol have been reported in the literature.⁷ The meso configuration has been assigned to one melting at 204-206°, although there is no direct proof that this is the proper configuration. This isomer is believed to be identical with isomer A, but again this could not be proven without

a direct comparison such as a mixed melting point. The dl isomer has been reported to melt at 96-97°, but no such compound was isolated from any of these reaction mixtures, and the compound separated from the cold alkali, isomer B, would apparently have a melting point about as high as isomer A if it could be obtained in a purer state. When compounds A and B were mixed, the melting point was depressed to 162-189°. Proof that compounds A and B were isomeric was obtained by heating each in alcoholic solution with p-toluenesulfonic acid. Under these conditions, a pinacolone rearrangement occurred to form compound (IV), 3, 3 bis-(p-hydroxyphenyl)-4-hexanone. The reaction mixture was an oil, but treatment with benzoyl chloride produced a dibenzoate (VII) melting at 173.5-175° from compound A and 174-175.5° from compound B (178° lit.).⁸ No depression was observed from a mixed melting point. A diacetate of compound A (VI) was also obtained, m.p. 84.5-86° (91° lit.).⁹

Dehydration of the isomeric mixture of A and B and purified A using the method of Dodds,¹⁰ refluxing in acetic anhydride-acetyl chloride solution, both produced dienestrol diacetate (III) in moderate yield, m.p. 117-119° (119-120° lit.).¹¹ Hydrolysis of the diacetate produced dienestrol (V) m.p. 230-231.5° vac. (227-228° lit.).¹² Since there was no difference in yields obtained on dehydration of the mixture of isomers and purified A, it may

be assumed that both isomers dehydrate with about equal ease although no attempt was made to dehydrate purified isomer B.

SUMMARY

Plated copper gauze cathodes have been found to be highly effective in bringing about the pinacol reduction of the ketone, p-hydroxypropiophenone. Mercury was found to be the most effective plating material. Both dl and meso isomers were produced in about equal quantities under a variety of conditions, with reduction in alkaline medium giving the best results. Results indicate that further work could be done profitably with these electrodes on other compounds which are subject to this type of reduction.

FIGURE I

EXPERIMENTAL

FIGURE II

APPARATUS.

Electrolytic cell.- The electrolytic cell consisted of the following: a 300 ml. beaker used as the cathode compartment, No. 15 rubber stopper, anode, cathode, mechanical stirrer, alundum diaphragm, amp. meter, volt meter, thermometer, and a source of variable direct current. This was assembled according to the diagram.

Cathode.- As the structural material for the cathode copper gauze of 20, 40, and 60 mesh per inch was used. In calculating the surface area of these cathodes, each wire had a certain amount of stretch when removed from the mesh, which was due to the overlapping of one wire over another to form the mesh. Thus, a factor was used for each to determine the actual length from the apparent or measured length. The factors were 1.1 for 20 mesh, 1.19 for 40 mesh, 1.25 for 60 mesh. The diameter of the 20 mesh wire was 0.0155 inches, the 40 mesh was 0.009 inches, and the 60 mesh was 0.007 inches.

The cathode of the desired mesh was shaped as a cylinder, with a diameter slightly less than the inside of the beaker and sewed together with fine copper wire. It was cleaned by dipping in a dilute solution of nitric acid, washed with water, and the metal of choice plated upon it. Lead was plated from a 5-10% solution of lead fluoborate at 1.4-3.0 amp. until the desired coating was obtained. For uniformity of lightly plated cathodes, they were all heavily plated then dipped in a 5% solution of copper sulfate. Lightly mercury plated cathodes were prepared by dipping the acid cleaned electrode in the desired solution of mercuric chloride. Solutions containing 2, 8, 12, 20 and 50 mg. of mercuric chloride were used. Heavily mercury plated cathodes were obtained from solutions containing 3 g. of mercuric chloride. Bismuth

cathodes were electroplated from solutions of bismuth nitrate and also from 5% solutions of bismuth subcarbonate in 33% perchloric acid. Nickel amalgam cathodes were prepared by first electroplating nickel heavily on the copper gauze at 2.2 amp. from a 10% aqueous solution of nickelous ammonium sulfate and 20 ml. of ammonium hydroxide. This was then dipped in a solution containing 50 mg. of mercuric chloride to obtain the amalgamated cathode. A silver amalgam was similarly prepared. The silver was first plated from a solution of silver cyanide which was prepared by dissolving silver nitrate in water, then neutralizing with potassium hydroxide, and then adding an excess of potassium cyanide.

Arsenic was electroplated from a solution of 3 g. sodium arsenate dissolved with a minimum amount of hydrochloric acid and then diluted to 400 ml. It was difficult to get a uniform plating of arsenic. Tin was electroplated from a solution containing stannous oxide, while antimony was plated from a solution, antimony oxide, dissolved in hydrochloric acid then diluted to 400 ml. All were electroplated by passing a current of 2.2 amp.

Cadmium was electroplated at 0.7 amp. from a 5% solution of cadmium oxide dissolved in perchloric acid and then diluted with water. In preparing the solution for thallium plating, 2 g. of thallic oxide was dissolved in a minimum amount of hydrochloric acid, then reprecipitated

by neutralizing with sodium hydroxide. This precipitate was then centrifuged, washed, and dissolved in a minimum amount of perchloric acid. This solution was diluted to 400 ml. and the thallium electroplated at 2.2 amp. Some of these electrodes were also dipped in a 3% solution of copper sulfate.

Anode.- Platinum was used as the anode in all reductions and electroplating with the exception of those using lead cathodes in sulfuric or phosphoric acid solution.

Diaphragms.- Alundum extraction thimbles 20 x 80 mm. and 34 x 100 mm. of dense porosity were used as the diaphragm and also served as the anode compartment. The method used in decreasing the porosity of the diaphragm for use in acid medium,¹³ was to allow the thimble to soak in a 20% solution of water glass for one hour, then remove it and place it in a 20% solution of sulfuric acid for one hour. At the end of this time, it was removed and allowed to dry for three hours, then stored in a 20% solution of sulfuric acid. This procedure was necessary only in the case of the larger thimbles.

Reduction

Acid medium.- The catholyte consisted of 10 g. of p-hydroxypropiophenone dissolved in 200 ml. of methanol, 70 ml. of water, and 6 ml. of concentrated sulfuric acid. The anolyte was 40 ml. of methanol,

14 ml. of water, and 1 ml. of concentrated sulfuric acid. The cathode and anode were as previously described. The reduction was allowed to proceed at 25° using a water bath to control the temperature, and stirred vigorously until current efficiency appeared to have dropped to zero. The initial current was 2.6 amp. at a potential of 8 volts. Upon completion of the reduction, the catholyte was neutralized with ammonium hydroxide, filtered and the methanol removed in vacuo. The resulting brown gummy material was extracted with ether, the ether solution dried with magnesium sulfate, filtered and then the ether evaporated in vacuo. The residue was crystallized from a minimum amount of acetic acid with care being taken not to heat over 35-40°, and the crystalline material separated by suction filtration. After drying, a yield of 44% with a m.p. 147-59° was obtained. This product was then recrystallized from acetic acid to obtain a m.p. 160-69°, however, there was a 50% loss of product. The purification of this crude product is best obtained by following the procedure described below, using 20% sodium hydroxide.

Alkaline medium.- The catholyte consisted of 10 g. of p-hydroxypropiophenone dissolved in 135 ml. of 2 N sodium hydroxide. The cathode was heavily plated mercury with platinum anode. The reduction was carried out by passing a current of 2.2 amp. at a potential of 7.5 volts for 47 minutes. The mixture was vigorously

stirred and the temperature of 25° maintained with the aid of water bath. At the completion of the reduction, the catholyte was neutralized with acetic acid, heated until the gummy precipitate solidified, then broken up and 10 g. of sodium chloride added. The precipitate was then filtered, washed with hot water, and dried. A crude yield of 9.9 g. (99%) of glycol, m.p. 148-59°, was obtained. This product was then extracted with cold 20% sodium hydroxide and after acidifying the sodium hydroxide insoluble material with acetic acid, a yield of 4.6 g. m.p. 171-79° was obtained. Upon extracting twice more, in a similar manner, a final yield of 3.1 g. of isomer A, m.p. 198-204° was obtained. The alkaline filtrates were combined, neutralized with acetic acid, and cooled. After filtering, washing, and drying 2.7 g. of isomer B, m.p. 161-73° was obtained. This was dissolved in reagent acetone, in which it was very soluble, and boiled down while isopropyl ether was added. This process was continued until all the acetone was evaporated with much care being taken to avoid bumping. The solvent was decanted while hot and the residue washed with isopropyl ether. A recovery of 2.2 g. with a m.p. 159-71° was obtained. No further purification of this portion of the product was attempted.

Buffered medium.- The catholyte consisted of 70 ml. of methanol, 30 ml. of water, 15 ml. acetic acid, 6 g.

sodium acetate, and 7 g. p-hydroxypropiophenone. The anolyte consisted of 4 ml. methanol, 4 ml. T-butyl alcohol, 8 ml. of water, 3 ml. acetic acid, and 1 g. sodium acetate. A heavily plated mercury cathode was used. The reduction was carried out by passing a current of 2.2 amp. at a potential of 15 volts for one hour. A temperature of 30° was maintained with the aid of a water bath and vigorous stirring. The pH at the start of the reaction was 5.6 and at the end 5.8. At the completion of the reduction, the catholyte was partly neutralized with sodium hydroxide and completed with sodium bicarbonate, and the methanol evaporated in vacuo. This resulting product was extracted with ether, dried with magnesium sulfate, and the ether evaporated in vacuo. Boiling toluene was used for separating the crystalline and non-crystalline products, however, due to the poor recovery of product, the toluene was evaporated in vacuo and acetic acid used to recover the remainder as in the acid reductions. A yield of 1.4 g. m.p. 165-177° was obtained.

3, 4 bis (p-methoxyphenyl) 3, 4 hexanediol.- The catholyte consisted of 10 g. p-methoxypropiophenone, 85 ml. of methanol, 13 ml. of acetic acid, 5 g. sodium acetate, and 30 ml. of water. The anolyte was 3 ml. of acetic acid, 1 g. of sodium acetate, 10 ml. of water, and 3 ml. of T-butyl alcohol. The reduction was carried out by passing a current of 2.2 amp. at a potential of 15 volts for 90 minutes. The temperature of 25° was maintained with the aid of water

bath. Due to the precipitation of the pinacol, the cathode became heavily coated after 30 minutes and interfered with the reduction by lowering current efficiency. At the completion of the reaction, the catholyte was neutralized with sodium hydroxide, the methanol evaporated in vacuo, and 100 ml. of water added. It was then heated to near boiling, 10 g. sodium chloride added, and upon cooling a precipitate formed which was filtered, washed with water, and dried. A yield of 2.6 g. with a m.p. 179-190° was obtained, however, no further purification was attempted.

Purification of the product.-

As a test for starting material, 2, 4 dinitrophenylhydrazine was used and when found present, it was removed by forming the water soluble semicarbazone. This required 4 g. of semicarbazide hydrochloride dissolved in a minimum amount of water and 6 g. sodium acetate dissolved in a minimum amount of methanol. These solutions were poured together, filtered, and added to 8 g. of the crude pinacol in a 100 ml. round bottom flask. This was refluxed for 75 minutes and then poured into 300 ml. of warm water. Upon cooling, a precipitate formed which was then extracted using cold 20% sodium hydroxide as the solvent. The insoluble material was filtered off using a sintered glass funnel, and the washing with 20% sodium hydroxide repeated twice more. The insoluble product was dissolved in water, the solution acidified with acetic acid, and the solid

which separated, filtered, washed with water, and dried to obtain 2.7 g. and a m.p. 195-204°. The alkaline filtrates were combined and neutralized with acetic acid, cooled and the resulting precipitate, isomer B, filtered, washed with water and dried. A yield of 2.1 g. with a melting point of 180-205° was obtained, but no further purification was attempted. Isomer A was recrystallized from reagent acetone with considerable loss, however, this was recovered by boiling off the acetone and adding isopropyl ether. The recrystallized isomer A melted at 190-200°.

Preparation of derivatives.-

Dienestrol diacetate.- The pinacol was acetylated and dehydrated according to the method of Dodds.¹⁴ In a 100 ml. round bottom flask, 10 g. of the pinacol was dissolved in 35 ml. of acetic anhydride and 4 ml. of acetyl chloride. After refluxing for three hours, the acetyl chloride and acetic anhydride were distilled off in vacuo. To the residue, 30-40 ml. of water was added, neutralized with sodium bicarbonate, and washed by decantation with water. The resultant product was dissolved in 25 ml. of ethanol and then boiled down to 15 ml. from which the dienestrol diacetate precipitated. The crude product was recrystallized from ethanol to yield 3.6 g. with a m.p. 117-119° (119-120° lit.).

Dienestrol.- The diacetate was hydrolyzed by refluxing with 7.5% sodium hydroxide for 14 hours to obtain

3, 4 bis (p-hydroxyphenyl) 2, 4 hexadine, (dienestrol) m.p. 215-224° in a 78% yield. This was recrystallized from isopropyl ether to give a m.p. 223.5-226° (227-8 lit.).¹⁶ with decomposition. When dried in vacuo and the capillary sealed a m.p. 230-231.5° without decomposition was obtained.

3, 3 bis (p-hydroxyphenyl) 4 hexanone, dibenzoate.-

One gram samples of isomer A and B were dissolved separately in 20 ml. of ethanol and to each solution 0.3 g. of p-toluene-sulfonic acid was added. After boiling for 20 minutes, these solutions were poured into 200 ml. of warm water and allowed to cool. The oily substance which separated was extracted with ether, dried with magnesium sulfate, and the ether evaporated in vacuo. The residue was dissolved in 10 ml. of potassium hydroxide and benzoyl chloride added dropwise with vigorous shaking. The dibenzoates so prepared were recrystallized from ethanol, to obtain 1.1 g. (65%) m.p. 171.5-174°, isomer A; 1.2 g. (70%) m.p. 171-174°, isomer B. The dibenzoate of B was recrystallized from benzene to give a product melting at 174-175.5° (178° lit.).¹⁷ No depression of melting point was obtained by the mixed melting point of the ketone dibenzoates obtained from isomer A and B.

3, 3 bis (p-hydroxyphenyl) 4 hexanone, diacetate.-

One gram of isomer A was dissolved in 20 ml. of ethanol and 0.3 g. of p-toluenesulfonic acid added. After boiling

for 20 minutes, the solution was poured into 200 ml. of warm water and cooled. This oily residue was extracted with ether, and the ether evaporated in vacuo, then refluxed with 15 ml. of acetic anhydride and 2 ml. acetyl chloride for 90 minutes. The acetyl chloride and acetic anhydride was distilled off in vacuo, 30 ml. of water added, and neutralized with sodium bicarbonate. This was then washed with water by decantation and the product recrystallized from ethanol to give approximately a 75% yield with a m.p. 84.5-86° (91° lit.).¹⁸

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ABSTRACT

The conditions for reduction of ketones to pinacols at plated copper gauze cathodes were studied. Mercury plated 40 and 60 mesh copper gauze was the most effective in both acid and alkaline medium. Lead plated copper gauze, the second most effective cathode, was followed by cadmium, silver-mercury, thallium, nickel-mercury, and bismuth. Tin, antimony, and arsenic did not produce the desired reaction. For acid medium 0.022% H_2SO_4 , as the electrolyte, gave the best results while in alkaline medium, 2 N NaOH gave the best results. The formation of the dl and meso isomers in about equal proportions were separated by cold 20% sodium hydroxide. Both isomers undergo dehydration and acetylation to give dienestrol diacetate which, upon hydrolysis, gives dienestrol. Heating the isomers in acid causes them to undergo the pinacolone rearrangement. By the Schotten-Baumann reaction, the dibenzoate was prepared and separated.