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ELECTROCHEMICAL REDUCTION OF KETONES TO PINACOLS

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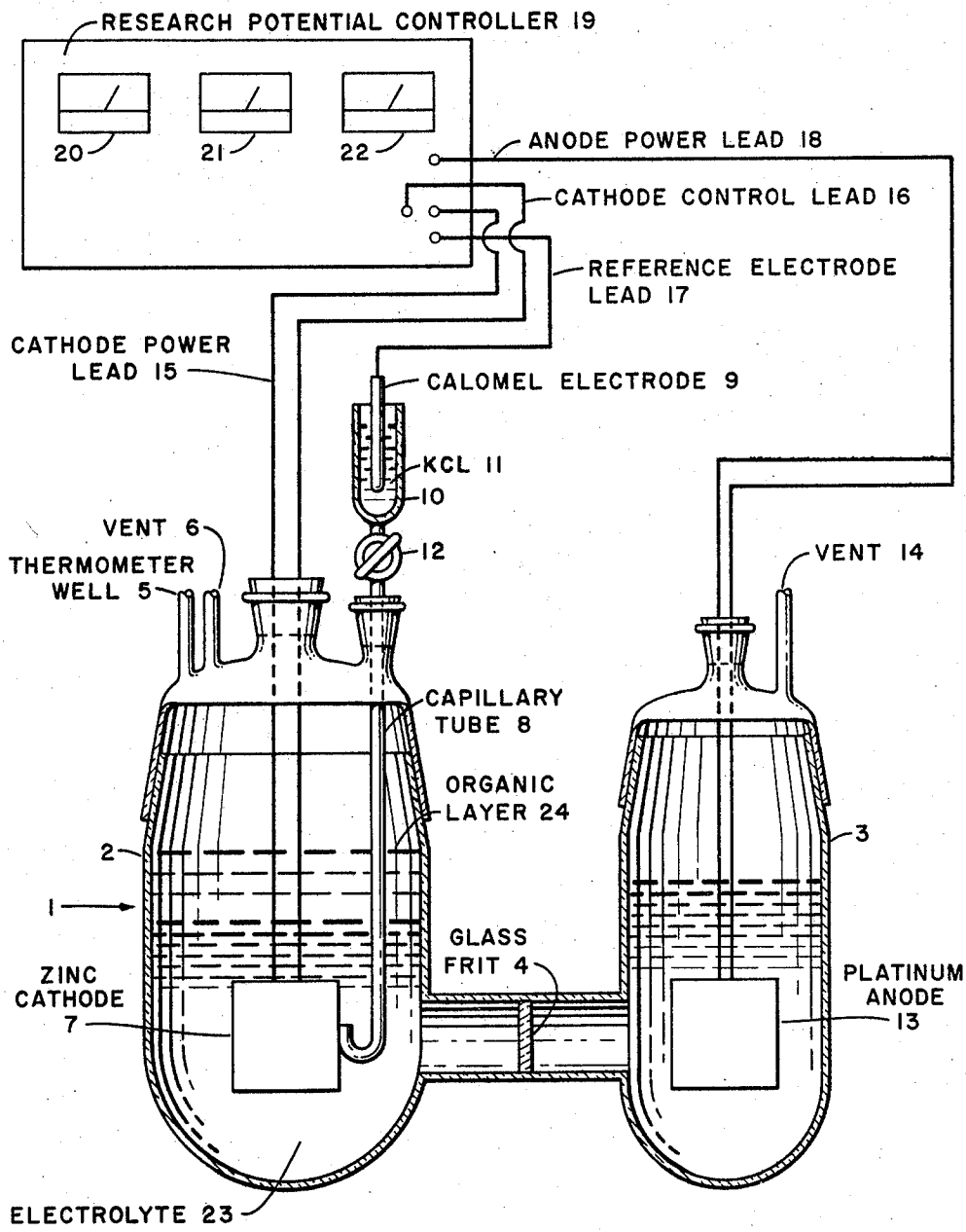


FIG. 1

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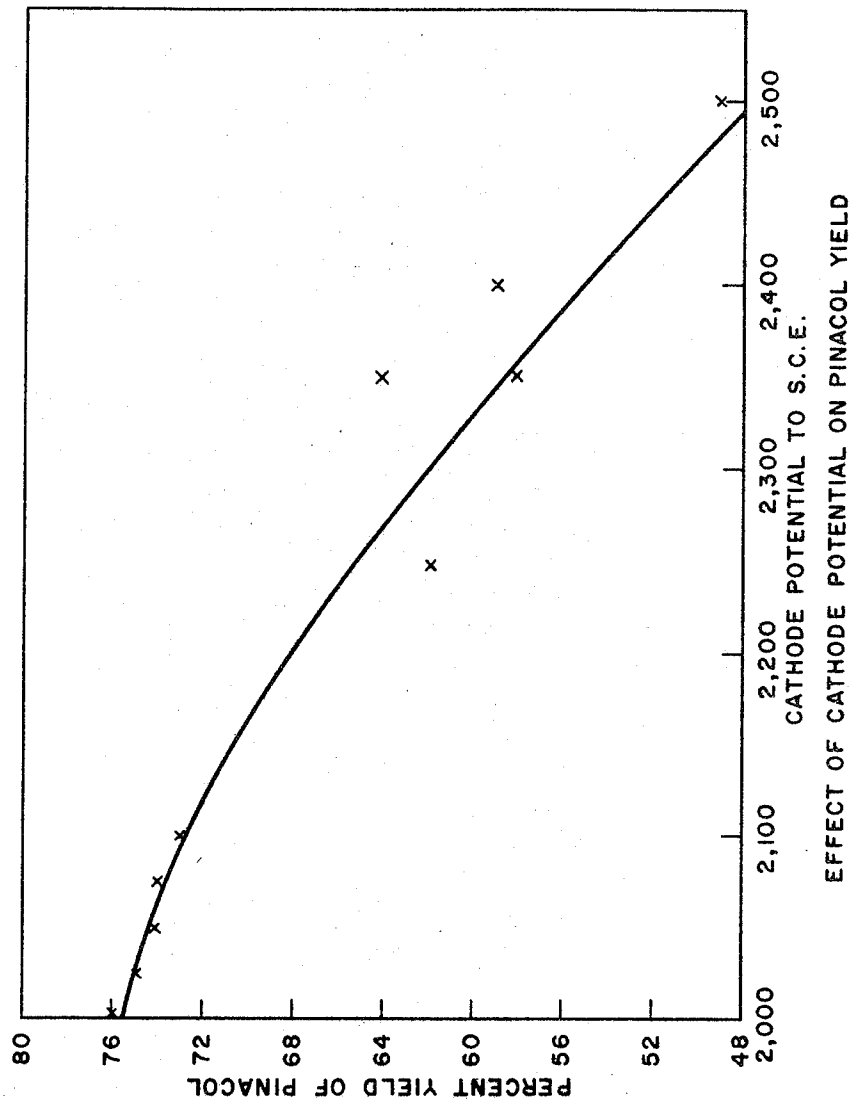


FIG. 2

EFFECT OF CATHODE POTENTIAL ON PINACOL YIELD

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ELECTROCHEMICAL REDUCTION OF KETONES TO PINACOLS

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U.S. Cl. 204—77 10 Claims

ABSTRACT OF THE DISCLOSURE

In the electrochemical reduction of ketones to pinacols, the selective conversion to pinacols is dependent upon controlling the potential to a maximum of 2100 millivolts vs. a saturated calomel electrode and is independent of current density.

This invention relates to an improvement in the process of producing pinacols from ketones by electrochemical reduction process.

It has long been known that ketones could be converted to pinacols by electrolytic reductive coupling reactions. An early German Patent 113,719 (1899), disclosed an electrolytic method for effecting the reductive condensation reaction whereby acetone is converted to pinacol (tetramethylene glycol). Numerous patents subsequent to that time have been devoted to improved electrodes, controlling temperatures, controlling pH and the like.

However, in all of these methods, the results have been erratic with pinacol yields varying widely. Even though yields as high as 65+% have been reported, these were from isolated runs and, as far as we have been able to ascertain, there has been no system developed which will consistently give yields of pinacols in excess of 70%.

It is an object of this invention to provide a method of constantly obtaining high yields of pinacols or glycols from ketones by the electrochemical reduction reaction in the presence of a catholyte.

We have found that for any given reaction, utilizing the prior art methods that maximum yields of pinacols are obtained if the current potential is controlled to 2100 millivolts or less as compared to saturated calomel electrode (S.C.E.).

In a preferred embodiment not only is the potential controlled as above, but we prefer to utilize a temperature in the range 5 to 15° C., an excess of ketone so as to form an aqueous layer and an organic layer, a pH greater than 7 and preferably greater than 9 and an electrode having an overvoltage at least as great as copper.

Baizer in U.S. Patent 3,193,478 teaches the use of electrochemical coupling of olefins, particularly reductive couplings of beta-hydrocarbyloxyacrylic acid ester, amide and nitrile, and has indicated a pH in the range 3–12, preferably 6 to 9.5, is useful in his process. However, we have been unable to obtain commercial yields of pinacols from ketones unless the electrolyte is in basic solution, e.g. greater than 7 and preferably greater than 9. Apparently there is no upper limit to the pH of the electrolyte; however, for economical reasons we would use sufficient catholyte to provide an aqueous solution having a pH in the range 9 to 13. Baizer also teaches the advantage of using a cathode having overvoltage at least as great as that of copper as determined in a 2 N sulfuric acid solution at a current density of 1 milliampere per square centimeter. We also prefer such cathodes. Examples of suitable cathodes then would include copper, copper coated with zirconium or other high overvoltage metals such as mercury, cadmium, tin, zinc, bismuth, lead, lead and copper or lead and tin, graphite, aluminum, nickel or combinations of these either as physical mixtures or alloys. We particularly prefer zinc since it is generally nonreactive with the common catholytes. Mercury, for example, tends to form an amalgam with Na and other electrolytes.

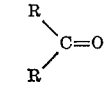
Bazier in U.S. Patent 3,193,477 in his coupling of olefinic compounds teaches the advantage of utilizing an excess of olefin over that which is soluble so as to form a supernatant layer over the electrolyte. The excess organic phase serves as an adsorbent for the product. We have also found this to be advantageous, and is a preferred method in our invention.

Chambers et al. in U.S. Patent 2,442,468 disclose the advantage of operating at a low temperature in electrochemical production of pinacols from ketones setting a maximum of 25° C. We can also use such a temperature; however, we have found that when the temperature exceeds about 15° C., the yield falls rapidly.

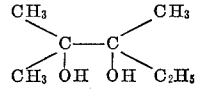
Most of the prior art on electrochemical reductive coupling has emphasized the necessity of controlling current density. However, we have found that the yield of pinacols from ketones is quite independent of current density, but rather is dependent upon electrode potential compared with S.C.E. We have also found that the general conditions for electrochemical reductive coupling of ketones is more critical than the prior art generally indicates.

The pinacol products of this invention are useful intermediates for more useful products. For example, the tetramethylene glycol product from the reductive coupling of acetone can be dehydrated to give 2,3 dimethyl butadiene, an ingredient for synthetic rubber, or such a glycol could be utilized for production of pivalic acid (see Z. Electrochem 7, 644 (1901); ibid 8, 783 (1902).

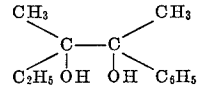
The process of this invention is applicable to ketones in general having the formula:



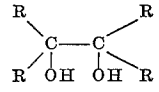
wherein each R can be an alkyl or aryl radical and such radicals substituted by a group which is not reducible under the conditions employed, e.g., halogen, carboxyl, substituted alkyl groups and the like. Such ketones include, but are not limited to acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, ethyl propyl ketone, acetophenone, benzophenone, and the like. Such ketones are abundantly disclosed in the art. Mixtures of ketones can also be treated to prepare mixed glycols. For example, if acetone is condensed with methyl ethyl ketone to form a glycol of the following formula:



or methyl ethyl ketone can be condensed with acetophenone to form the glycol:



Thus, the glycols formed by the electrochemical reductive method of this invention will correspond to the general formula:



wherein each R is an alkyl or aryl radical or such radicals substituted with halogen, carboxyl, alkyl and the like.

As previously indicated, these electrochemical reductive coupling reactions are well known in the art.

In describing out invention, reference will be made to the drawings of which:

FIGURE 1 is a schematic illustration of a typical electrolytic cell suitable for carrying out our invention, and

FIGURE 2 is a graph wherein cathode potential to S.E.C. is plotted against percent yield of pinacol from acetone.

Referring to FIGURE 1, electrolytic cell **1** comprising compartments **2** and **3** with said compartments being separated by glass frit **4** was utilized for electrochemical reductive coupling of ketones. Compartment **2** had an opening **5** for a thermometer and vent **6**. In compartment **2** was a zinc cathode **7** and a capillary tube **8** which was turned up at the bottom and arranged to rest against the cathode. This provided for a constant distance, e.g., glass thickness, between the zinc cathode and the reference electrode. The capillary tube **8** was filled with KCl to conduct the current to the calomel electrode **9**. The calomel electrode was placed in a vessel **10** which was partially filled with KCl **11**. The stop-cock **12** was a convenient way to hold the KCl in the vessel **11** and by rotating the stopcock it was coated with KCl to couple the circuit to the capillary tube. Compartment **3** contained the anode **13**, in this case platinum was used as the anode. This compartment was also provided with a vent **14**. The cathode power lead **15**, cathode control lead **16**, reference electrode lead **17** and anode power lead **18** were connected to a Research Potential controller or potentiostat **19**. This potentiostat had applied voltage indicator **20**, amphere indicator **21** and potential reference indicator **22**. Such research potential controllers are sold by the Magna Corporation of California under the trademark "Anotrol." Either the 4100 or 4700 models are suitable for potential control. Any suitable power supply can be utilized.

In coupling the ketone, sufficient electrolyte **23** is utilized to cover the cathode, the open end of the capillary tube and the anode. Excess ketone is placed in compartment **2** to form an organic phase **24** on top of the electrolyte. The entire cell is then immersed in a constant temperature bath, and then the desired temperature is obtained; the current at controlled potential is applied.

To illustrate the invention, acetone was utilized as the ketone, and the product was pinacol and isopropanol. A 2 N sodium hydroxide solution was utilized as the electrolyte.

A Perkin-Elmer Model 154 gas chromatograph, with a standard carbowax column was used to determine acetone, isopropanol and pinacol quantitatively. Gas chromatograph analysis showed the only products formed were isopropanol and pinacol and that the decrease in acetone was accounted for by the appearance of these two products.

Recovery of pinacol is a fairly simple procedure. Excess sodium hydroxide is added to the already alkaline electrolyte to get a strong phase separation with almost all the pinacol going into the acetone phase. The two phases are split by means of a separatory funnel and the acetone evaporated at low temperatures leaving the pinacol in a concentrated aqueous solution. The solution is then frozen with Dry Ice and filtered. The solid product was obtained as a white pinacol hydrate ($C_6H_{14}O_2.6H_2O$), which proved to be 99% pure.

EXAMPLE I

Several runs were made wherein acetone was converted to pinacol at 10° C.±1° C. at controlled potential. The reaction was carried out in the presence of a 2 N solution of NaOH with an excess of acetone present throughout the runs. When the cathode was polarized to a maximum potential of 2100 mv. (active) to S.E.C., the pinacol yield ranged from 73 to 76 percent, and this was independent of current density. The data are shown in Table I, and are plotted in FIGURE 2.

TABLE I

Run No.	Cathode, mv., Potential SCE	Current Density, ma./cm.^{2}	Percent Yield, Pinacol
1	2,000	7.50	76
2	2,025	3.75	75
3	2,025	30.00	75
4	2,025	30.00	71
5	2,050	7.50	74
6	2,075	15.00	74
7	2,100	7.5	73
8	2,100	15.0	73
9	2,250	15.0	62
10	2,350	30.0	64
11	2,350	30,0	58
12	2,400	15.0	59
13	2,500	30.0	49

From Table I, it is readily seen that pinacol yield was in excess of 70% when the cathode potential was held to 2100 or below, and this was independent of current density.

EXAMPLE II

Several runs were made using the cell of FIGURE 1 wherein the potential vs. SCE was held at about 1875, but the temperature was varied. At 5° C. some pinacol precipitated on the cathode, and thus this is considered a preferred minimum temperature. When the temperature exceeded about 15° C., the pinacol yield started to fall rapidly to 30% at 30° C. Therefore, we prefer a temperature range from 5 to 15° C. However, at any temperature, the yields were better when the cathode potential was held to a maximum 2100 millivolts vs. SCE.

EXAMPLE III

A number of runs were made using the procedure of Example I to determine the effect of potential on distribution of current between isopropanol and pinacol. The results are shown in Table II.

TABLE II

Run No.	Percent Current to Isopropanol	Percent Current to Pinacol	Ratio Pinacol to Isopropanol	Potential, mv. vs. SCE	Current Density, ma./cm.^{2}	Percent Yield Pinacol
14	28	46	1.6	2,000	7.50	76
15	21	33	1.6	2,025	3.75	75
16	26	40	1.5	2,025	3.75	75
17	23	34	1.5	2,050	7.50	74
18	20	29	1.5	2,075	15.0	74
19	27	37	1.4	2,100	7.50	73
20	25	35	1.4	2,100	15.0	73
21	33	29	0.9	2,350	30.0	64
22	38	27	0.7	2,350	30.0	58
23	13	9	0.7	2,400	15.0	59
24	32	16	0.5	2,500	30.0	49

From Table II it can be seen that the controlled potential resulted in a greater percent of the current going to pinacol than that going to isopropanol resulting in the higher yields of pinacol.

In view of the prior art, we believe it was indeed surprising to find that cathode potential is the controlling factor in efficiency in electrochemical reductive coupling of ketones to pinacols.

Having thus described our invention, we claim:

1. In the electrochemical reductive coupling of ketones to form pinacols in a basic aqueous solution, the improvement comprising controlling the cathode potential to a maximum of 2100 millivolts vs. saturated calomel electrode.

2. The improvement of claim **1** wherein the ketone is present in an amount in excess of the solubility of said ketone in said aqueous solution throughout the reaction time.

3. The improvement of claim **2** wherein the pH of said aqueous solution is at least 9 and the temperature of the reaction is maintained in the range of about 5 to about 15° C.

4. The improvement of claim **3** wherein the ketone is acetone.

5. The improvement of claim 3 wherein the ketone is methyl ethyl ketone.

6. The improvement of claim 3 wherein the ketone is diethyl ketone.

7. The improvement of claim 3 wherein the ketone is acetophenone.

8. The improvement of claim 3 wherein the ketone is benzophenone.

9. The improvement of claim 3 wherein the ketone is a mixture of at least two ketones.

10. The improvement of claim 3 wherein the ketones are methyl ethyl ketone and acetophenone.

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