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[54] ELECTROCHEMICAL PRODUCTION OF PINACOLS

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[51] **Int. Cl.. C07b 29/06;** C07c 29/00; C07c 31/20
[58] **Field of Search**............ 204/59 R, 72, 73 R, 76, 204/77

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[57] ABSTRACT

Pinacols are prepared by electrolytic hydrodimerization of carbonyl compounds in non-compartmented cells using a mixture of from 5 to 75% by weight of the carbonyl compound, from 5 to 90% by weight of the alcohol corresponding to the carbonyl compound, from 0.1 to 3% by weight of a quaternary ammonium salt and from 0 to 30% by weight of water.

3 Claims, No Drawings

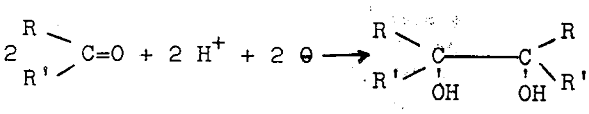
ELECTROCHEMICAL PRODUCTION OF PINACOLS

This application discloses and claims subject matter described in German Pat. application No. P 23 43 **054.8,** filed Aug. 25, 1973, which is incorporated herein by reference.

The invention is concerned with a new and particularly advantageous process for the electrochemical manufacture of pinacols.

It is known that organic carbonyl compounds, especially aldehydes and ketones, can be dimerized, with simultaneous hydrogenation, to the so-called pinacols, that is to say to derivatives of the alkylene glycol.

This hydrodimerization can only be carried out electrochemically on a cathode whereof the hydrogen overvoltage is not too low, or by means of a suitable reducing agent. It cannot be carried out under catalytic hydrogenation conditions. Photochemical synthesis of the pinacols proves rather unsatisfactory, in particular with regard to the energy yield. In the electrochemical synthesis of a pinacol, the hydrogen is provided by the protons of the solvent or of an added acid:



$$2\,\begin{matrix}R\\R'\end{matrix}\!\!>C{=}O + 2\,H^{+} + 2\,\ominus \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>\underset{OH}{C}-\underset{OH}{C}<\!\!\begin{matrix}R\\R'\end{matrix}$$

It is also known that the formation of pinacols from aromatic or aromatic/aliphatic carbonyl compounds gives high yields, whilst only moderate to poor yields of the pinacol are to be expected with purely aliphatic compounds.

This situation is related to the stability of the radical intermediates.

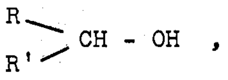
Starting from acetone, tetramethylethylene glycol, referred to as "pinacol," is obtained. This compound is converted into pinacolene or into 2,3-dimethylbutadiene by acid-catalyzed elimination of one or two molecules of water, respectively.

Both these products derived directly from pinacol, and pinacol itself, are interesting intermediates for the synthesis of polymers, pharmaceutical products and pesticides. However, a broad use of these products has hitherto been prevented by the fact that only unsatisfactory methods of manufacture were available.

One process for the manufacture of pinacol consists, for example, in reacting acetone with amalgams of aluminum, magnesium or sodium. This process is still being used to manufacture pinacol on a small scale. The process produces a great deal of isopropanol as a by-product and the degree of utilization of the metal is relatively low, so that the resulting costs are high. Furthermore, the salts produced are an objectionable ballast. While the lastmentioned disadvantage is avoided in direct electro-reduction on lead, lead-copper alloy or lead-tin alloy cathodes in electrolytes containing sulfuric acid or in alkaline electrolytes, this process has not found industrial acceptance, because it suffers from various disadvantages. Thus, the formation of highly toxic lead organyls ("lead oils") as by-products at the cathode cannot be avoided. Furthermore, a compartmented cell is required, since otherwise acetone and pinacol undergo oxidative degradation at the Pb/PbO_2 anode. In addition, only poor current efficiencies are attainable. Further, the electrolyte has to be neutralized before working up to prevent the acid-catalyzed elimination of water to give pinacolene or dimethylbutadiene, and this neutralization produces large amounts of salts. It is also a disadvantage that some of the acetone is reduced to the valueless by-product isopropanol and that the solutions contain a large amount of water which must in part be evaporated during working up.

It is an object of the present invention to provide a direct electrochemical process for the manufacture of pinacols from carbonyl compounds which avoids the above disadvantages. This object is achieved by the process according to the invention.

According to the process of the invention, pinacols of the formula II, in which R is hydrogen or a hydrocarbon radical of one to six carbon atoms and R' is a hydrocarbon radical of one to six carbon atoms are manufactured by electrolytic hydrodimerization of carbonyl compounds of the formula I in non-compartmented cells, using for the electrolysis a mixture which contains from 5 to 75% by weight of the carbonyl compound, from 5 to 90% by weight of the alcohol corresponding to the carbonyl compound, of the formula



$$\begin{matrix}R\\R'\end{matrix}\!\!>CH-OH\ ,$$

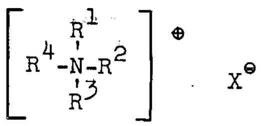
from 0.1 to 3% by weight of a quaternary ammonium salt and from 0 to 30% by weight of water.

The hydrocarbon radicals can be straight-chain or branched radicals and can be saturated or unsaturated. Methyl, ethyl, propyl, butyl, isopropyl, isobutyl, hexyl and cyclohexyl may be mentioned as examples of hydrocarbon radicals.

Examples of suitable carbonyl compounds are acetone, acetaldehyde, methyl ethyl ketone, diethyl ketone, methyl isopropyl ketone and methyl cyclohexyl ketone. The use of acetone and of the corresponding alcohol isopropanol is of particulr interest in industry.

The mixture to be subjected to electrolysis contains from 5 to 75% by weight, preferably from 10 to 40% by weight, of the above carbonyl compound. It also contains from 5 to 90% by weight, preferably from 20 to 80% by weight, of the alcohol corresponding to the carbonyl compound.

Suitable quaternary ammonium salts, of which from 0.1 to 3% by weight, preferably from 0.5 to 1% by weight, are present in the mixture to be subjected to electrolysis, are, for example, compounds of the formula



$$\left[\begin{matrix} & R^1 & \\ R^4- & N & -R^2 \\ & R^3 & \end{matrix}\right]^{\oplus} X^{\ominus}$$

in which the radicals R are alkyl, such as alkyl of one to six carbon atoms, for example methyl, ethyl, n-propyl, i-propyl or n-butyl, aryl, such as phenyl, or aralkyl, such as benzyl, and X is an anion, for example a sulfate, alkylsulfate, phosphate, carbonate, arylsulfonate such as tosylate, tetrafluoroborate, hexafluosilicate or perchlorate anion.

Particularly suitable conducting salts of this type are tetraethylammonium ethyl-sulfate, tetraethylammonium sulfate and tetrabutylammonium tetrafluoborate. Within the stated range, the concentration of these salts should be kept as low as possible to simplify the isolation of the pinacol and avoid its anoidic degradation.

Since an electrosynthesis can be carried out with economical current/voltage data even at minimal concentrations of the conducting salt if cells with closely spaced electrodes are employed, in DT-OS (German published application) No. 1,804,809, and in J. Appl. Electrochem. 2, 59 (1972) is particularly suitable for the process of the invention. In the present instance, the electrode spacing in these cells in suitably from 0.1 to 1.0 mm, preferably from 0.2 to 0.5 mm.

In principle, it is possible to employ as the cathode material any metal of medium or high hydrogen overvoltage, that is to say Cu, Ag, Cd, Zn, Sn, Pb, Tl and Hg, as the pure metals or in the form of their alloys. However, particularly advantageous cathode materials are graphite, carbon and graphite-filled plastics. Examples which may be mentioned are the commercially available electrode carbons of type LEK or EXN as supplied by Conradty, Nuremberg, West Germany, or of type DIABON N, BS 70 or P 127 from Sigri, Meitingen, West Germany or BASCODUR from Raschig, Ludwigshafen, West Germany. The carbon cathodes should preferably be cleaned carefully before the electrolysis, for example by rinsing them with concentrated hydrochloric acid and/or by brushing them with pure quartz powder. The carbon electrodes, which are usually porous, should preferably be stored in distilled water. The current efficiency can be increased by depositing a very thin layer, namely from 1 to 1,000 atom layers, preferably from 30 to 100 atom layers, of certain metals, such as Hg, Pb, Cu, Ag or Au, individually or as mixtures, on the cathode prior to the electrolysis. For this purpose, the electrodes, in the ready-assembled cell, are dipped into a dilute acidified aqueous solution of the corresponding metal salt such as $Pb(NO_3)_2$, $HgSO_4$, $CuSO_4$, $AgNO_3$ or $AuCl_3$, and the metal is deposited at current densities of from 0.1 to 1 A/dm^2 for the calculated period of time, whilst circulating the solution. The metals are more probably distributed over the surface as islands at selected points than as a coherent layer.

A suitable anode material is above all lead dioxide, preferably as a composite electrode on base surfaces of graphite, carbon, lead titanium or tantalum. Other oxide anodes, such a Fe_3O_4, MnO_2, Tl_2O_3 or RuO_2 (on Ti) can also be employed, as can gold, graphite, carbon and the platinum metals. The use of graphite anodes is particularly advantageous. Since graphite cathodes are also preferred, the bipolar electrodes are thus conveniently simple discs or plates of graphite, carbon or graphite-filled plastics. At pH values above 7, and in particular above 10, it is also possible to employ metals which can be passivated, such as Fe, Co, Ni or chrome nickel steel, as the anode material in the process according to the invention. A preferred bipolar electrode consists of graphite plates or carbon plates which have optionally been coated with lead dioxide (100 to 500 μ) on the anode side, or to which thin foils of, for example, Ti or Ni have been glued by means of a graphite-filled adhesive.

The current density used in the process according to the invention is not critical and is, for example, from 0.1 to 100 A/dm^2, preferably from 5 to 25 A/dm^2.

The temperature is suitably maintained at from 0°to 50°C. Whilst low temperatures increase the current yield, they entail technical complications. For this reason, temperatures of from 20°to 35°C are preferably used.

When using carbon cathodes, the pH proves to have little influence and can be selected to be from 1 to 14. If the pH is not regulated externally, it assumes a value of from 2 to 4 during the electrolysis.

Movement of the bath is advantageous, and is essential when using a capillary gap cell. Good convection is achieved by circulating the electrolyte by means of a pump. The rate of flow parallel to the electrodes is preferably set to values of from 1 to 30 cm per second.

It is advantageous to continue the electrolytic hydrodimerization until final concentrations (or stationary concentrations, in continuous operation) of pinacol of from 1 to 30% by weight, preferably from 5 to 20% by weight, have been reached. Separating the unconverted carbonyl compound from the product presents no problems.

In working up the material issuing from the electrolysis, it is advisable first to adjust the pH to 7 by adding a little sodium hydroxide solution, so as to avoid the acid-catalyzed rearrangement to pinacolone during working up. The unconverted acetone and isopropanol are stripped off, for example under reduced pressure. The solution which remains is cooled, for example to 0°C whilst stirring, if necessary after addition of water. The pinacol crystallizes out as pinacol hexahydrate, which is filtered off and washed with a little ice water. The mother liquor contains the quaternary ammonium salt and can be recycled to the electrolysis, if appropriate after first extracting it with ether or methylene chloride to remove water-soluble by-products.

Current efficiencies based on pinacol of more than 50% can be achieved by the process of the invention. Particularly high current efficiencies are obtained when from 1 to 30% by weight, preferably from 3 to 10% by weight, of dioxane is added as the co-solvent. These current efficiencies are substantially in excess of the values of 37% (U.S. Pat. No. 2,485,258) and 44% (U.S. Pat. No. 2,422,468) hitherto given in the literature for the synthesis of pinacol. The addition of methanol, in concentrations of from 5 to 70% by weight, preferably from 10 to 40% by weight, to the reaction mixture proves to be particularly advantageous when graphite anodes are used.

The process according to the invention can be carried out batchwise or continuously. In continuous operation, the reaction mixture is circulated continuously through the cell (and, preferably, through a heat exchanger).

The process of the invention is carried out in a non-compartmented cell. The preferred anode process is the dehydrogenation of the alcohol, for example in accordance with the equation

$$CH_3—CHOH—CH_3 \rightarrow CH_3—CO—CH_3 + 2\ H^+ + 2\ \theta$$

Thus a part of the ketone which is converted at the cathode is produced from the alcohol at the anode. If the formation of pinacol takes place cathodically with high yield, which is desirable, a part of the ketone to be converted is introduced in the form of the corresponding alcohol in the process according to the invention. In this case, the acetone is consumed at the cathode, is a single-electron reaction, more rapidly than it can be replaced from the isopropanol, at the anode, in a two-electron reaction. On the other hand, if there is a high cathodic subsidiary yield of alcohol, it suffices if relatively little of the alcohol is introduced initially. In any case, net production of this undesired by-product can be prevented completely. Because the alcohol is available in sufficient concentration at the anode, the anodic reverse decomposition of the pinacol to the carbonyl compound, an anodic reaction which normally takes place, is — surprisingly — substantially prevented.

In addition to the high current efficiency, the process according to the invention has yet other advantages over the known processes. Thus the production of salts, which is unavoidable when the acids are neutralized, does not arise. Because of the low concentration of the ammonium salts in the mixture, there is no solubilizing effect of the pinacol. Since the solutions contain relatively little water, only little energy is required to concentrate the material issuing from the electrolysis.

EXAMPLE 1

The cell used is a capillary gap cell consisting of a stack of circular horizontal plates of DIABON N (Messrs. Sigri) electrode carbon, the discs being of 117 mm diameter and 10 mm thickness. The plates are wired bipolar in series. The anode side of the plates is provided with a 300 μ thick layer of PbO_2 anodically deposited from lead nitrate solution. The interior of the stack of plates bears a 30 mm hole, so that the effective electrode surface is 1 dm^2. A spacing of 0.25 mm is maintained between the plates by radially applied polyester strips. The stack of plates is suspended from the cover of the cell. The current is supplied at the ends of the bipolar stack of plates, via an insulated middle axial in the case of the bottom end, or directly in the case of the upper end. The reaction solution is pumped through a union on the cover of the cell into the center of the stack of plates, flows radially outward through the capillary gaps and is returned into the center of the stack of plates via a heat exchanger. The cell, which is further provided with a thermometer, a glass electrode and an off-gas pipeline, is described German laid-open specification No. 1,804,809.

At the start of the electrolysis, 1 kg of a mixture consisting of 50% by weight of acetone, 39.5% by weight of isopropanol, 10% by weight of water and 0.5% by weight of tetraethylammonium ethyl sulfate is introduced into the cell. A total of 138.6 ampere hours is passed through the system at a current density of 10 A/dm^2, a temperature of 20°C and a pH of from 2 to 3, (which maintains itself automatically), whilst circulating the electrolyte at 7.5 liters per minute. Since the stack consists of 6 pairs of electrodes, this corresponds to an electrolysis time of 2.30 hours. In this way, the acetone initially introduced is theoretically converted to the extent of 60%. During the electrolysis, the potential of 55 volt (9.2 volt per electrode pair) remains practically constant.

After termination of the electrolysis, the liquid is colorless. After taking a sample to determine the acetone (with $NH_2OH.HCl$) and adjusting the pH to 7.0 by adding 4.3 ml of 1 N NaOH solution, the acetone and the isopropanol are stripped off in a rotary evaporator at 40°C under 100 mm Hg. A further 50 g of water are added to the residue and the mixture is cooled to 0°C. Hereupon, pinacol hydrate crystallizes out and is filtered off quickly and rinsed with a little ice water. 98.5 g of a pure white crystalline product containing 53% of pinacol, and thus having a composition close to that of pinacol hexahydrate, are obtained. A further 2.5 g of pinacol can be extracted from the mother liquor by means of ether. Accordingly, the total pinacol yield is $52.2 + 2.5 = 54.7$ g. This corresponds to a current efficiency of 20.3%. Assuming anodic dehydrogenation of isopropanol with 100% current efficiency, a current efficiency of 70.4% for its cathodic formation can be calculated from the acetone balance. 6.6 g of 2-methylpentane-2,4-diol were isolated as a high-boiling by-product from the above ether extract. The subsidiary yield of isopropanol had no nett effect in the process according to the invention. The pinacol hexahydrate isolated as the main fraction melts at 44°C (literature value: 45.4°C).

EXAMPLE 2

The electrosynthesis described in Example 1 was repeated, varying the acetone : isopropanol ratio and in some cases also varying the water content in the batches. The table which follows lists the concentrations of the components, the amounts of current, the current efficiencies based on pinacol, designated "CE," and the cell potentials (for six electrode pairs), designated "U_c." The results show that optimum current efficiencies based on pinacol are obtained at low acetone concentrations and high isopropanol concentrations. In all experiments, the current density of 10 A/dm^2, the temperature of 20°C, and the conducting salt concentration of 0.5% of tetraethylammonium ethyl-sulfate ($= NEt_4.EtSO_4$) were kept constant.

A subsidiary yield of 2-methylpentane-2,4-diol of 26.3 and 22.8 was isolated respectively from the two batches of lower water content at the beginning of the table.

Table

(1 kg batches)

Composition (% by weight)				Electrolysis data	
Acetone	Isopropanol	H_2O	CE (%) based on pinacol	U_c (V). (6 electrode pairs)	Q (Ampere hours)
* 84.5	10	5	5.6	49	136.8
74.5	20	5	6.8	51	137.8
65	15	19.5	14.3	42	122.5
50	39.5	10	20.3	55	138.6
40	49.5	10	23.8	56	138.7
30	59.5	10	27.5	66	111
20	69.5	10	33.9	60	106.1 per 1.5 kg
10	79.5	10	41.2	64 at 5 A/dm^2	111 per 3 kg

* Comparative run

EXAMPLE 3

The temperature and the current density were varied under the experimental conditions mentioned in Example 1. The results are listed in the table.

Table

	(Batches containing 1% of $NEt_4.EtSO_4$)		
t (°C)	J[A/dm²]	CE (%) based on pinacol	U_c [V] (6 electrode pairs)
20	10	20.3	41
10	10	23.8	49
0	10	29.8	58
20	25	22.7	75.5
20	40	24.8	115

It can be seen that the current efficiency rises substantially with decreasing temperature and increasing current density.

EXAMPLE 4

The influence of dioxane as a co-solvent was examined in more detail in the series of experiments which follows. The solutions contained 40% of acetone, 2.5% of water, 1% of $NEt_4.EtSO_4$ and the amounts of dioxan listed in the table which follows, the remainder consisting of isopropanol. The penultimate column compares the initial potential with the final potential. The experiments showed a slight tendency for the potential to rise, and indicated the formation of small amounts of an acid by-product, but no covering layers were detectable on the electrodes at the end of the experiment. 138.7 ampere hours were used per kg of batch, corresponding to a theoretical conversion of 60%. The current density, temperature and other conditions of electrolysis were the same as in Example 1.

% by wt. of solvent	CE % based on pinacol	U_c [V] (6 electrode pairs)	Color of the crude product after stripping
27 dioxane	51	54/62	Yellow
20 dioxane	45	47/60	Light yellow
10 dioxane	43	53/59	Light yellow
5 dioxane	39	50/58	Light yellow
2 dioxane	37	52/58	Light yellow
1 dioxane	27	52/57	Light yellow

EXAMPLE 5

The cathode materials listed in the first column of the table which follows were employed in order to investigate the influence of the cathode material. In other respects, the experimental conditions and the cell were identical with those in Example 1.

Table

	(1 kg batches)		
Cathode	Atom layers of foreign metal	CE (%) based on pinacol	U_c [V] for 6 electrode pairs
DIABON N (Messrs. Sigri)	—	20.3	55
DIABON N	30 Hg	27.5	55
DIABON N	100 Hg	29.1	54
DIABON N	300 Hg	26.8	54
DIABON N	100 Pb	27.7	55
CONRADTY LEK	—	19.5	55
CONRADTY LEK	100 Hg	31.1	54
BASCODUR (Raschig)	—	21.5	54
SIGRI BS 70	—	15.0	53

In some experiments, the cathode was coated with foreign metals prior to the electrolysis. Hg was deposited from a solution of 100 g of $HgSO_4$ and 60 g of H_2SO_4 per liter at 0.5 A/dm², whilst circulating the solution. This required a deposition time of 6 seconds for 100 atom layers of Hg, if it is assumed that one atom layer contains 10^{15} atoms per cm². The lead was deposited from an acid lead tetrafluoborate bath, using the same current density.

Comparison of the unmodified types of graphite shows that BASCODUR and DIABON N give more advantageous results than LEK or BS 70. However, coating LEK with Hg gives better current efficiencies that coating DIABON N.

EXAMPLE 6

The experiments which follow and are summarized in the table were carried out in the cell described in Example 1. The conditions of electrolysis were the same as in Example 1, but the conducting salt and the water concentration were varied. In the case of the experiments with low water content and the experiments with virtually anhydrous systems, 2-methylpentane-2,4-diol was again obtained as a by-product, in the yields shown in the table. The results show that the best current efficiencies based on pinacol are obtained in the presence of tetrabutylammonium tetrafluoborate (= $NBu_4.BF_4$) with 2.5% of water. These conditions also resulted in relatively little of the by-product 2-methylpentane-2,4-diol.

Table

				(1 kg batches)				
Conducting salt (%)	% H_2O	% Ac	% IP	Pinacol g	Pinacol CE (%)	2,4-Dimethylpentane-2,4-diol (g)	Q (ampere hours)	U_c [V]
0.5 $NEt_4.EtSO_4$	—*	59.5	40	51	16.9	24	137.7	60
"	2.5	57	40	50.5	17.2	20	132	57
"	19.5	40	40	53.4	18.6	—	138.5	52
1.0 $NBu_4.BF_4$	—**	59	40	85.5	28.6	10.3	136.5	54
"	2.5	56.5	40	89.8	31.0	10.8	132	49
"	19.5	40	40	68.5	22.5	—	138.5	47

*Water content at end of experiment: 0.12%
**Water content at end of experiment: 0.23%

EXAMPLE 7

1 kg of a reaction mixture composed of 50% of methyl ethyl ketone, 39.5% of sec. butanol, 10% of water and 0.5% of $NEt_4.SO_4$ was introduced into the capillary gap cell described in EXample 1, but consisting of four electrode pairs. The DIABON-N cathodes were coated with "100 atom layers" of mercury — as in Example 5 — prior to the experiment. The electrolysis was carried out at 10 A/dm^3 and 20°C until an amount of current of 111.8 ampere hours had been passed through, corresponding to a theoretical conversion of 60%. Accordingly, the electrolysis time was 2.8 hours. During the electrolysis, the cell potential rose from 50.5 to 55 volt. The pH at the end of the electrolysis was 5.0. For working up, the low-boiling constituents of the electrolyte were distilled off under reduced pressure. 77.2 g of a brown crude product were left; this was examined directly by gas chromatography. It contained 12.3% = 9.5g of pinacol (1,2-dimethyl-1,2-diethyl glycol), corresponding to a current efficiency of 3.1%.

EXAMPLE 8

The capillary gap cell described in Example 1 consists in this case of a stack of DIABON-N discs (6 × 1 dm^2, $d = 250\mu$). Thus, in this experiment, the anode is also composed of graphite. At the start of the electrolysis, 1 kg of reaction mixture A or B is introduced into the cell.

A	50% of acetone 39% of isopropanol 10% of water 1% of $NEt_4.EtSO_4$
B	50% of acetone 20% of methanol 19% of isopropanol 1% of $NEt_4.EtSO_4$

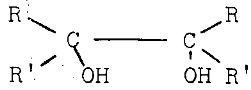
These reaction mixtures are reacted as in Example 1, at 10 A/dm^2, 20°C and a pH of from 3 to 4, which maintains itself automatically, the amount of current being 138.6 ampere hours (corresponding to an electrolysis time of 2.3 hours and a theoretical conversion of 60%).

In case A, the potential assumes a total value of 44 volt. During the electrolysis, the anodic graphite suffers some attack and the electrolyte turns black due to dispersed graphite particles. After the electrolysis, a total amount of 4.5 g of graphite dust can be isolated. The current efficiency based on pinacol is found to be 21.5% and the energy requirement for pinacol formation is found to be 15.5 kWh/kg.

In case B, the potential is only 37 volt (at the 6 electrode pairs). During the electrolysis, the anodic graphite is hardly attacked and the liquid remains almost clear. The graphite dust filtered off after the electrolysis weighs 0.1 g. Pinacol is formed with a current efficiency of 19.0%. The energy required for pinacol formation is 14.7 kWh/kg.

We claim:

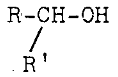
1. A process for the manufacture of pinacols of the formula



in which R is hydrogen or a hydrocarbon radical of one to six carbon atoms and R' is a hydrocarbon radical of one to six carbon atoms, by electrolytic hydrodimerization of carbonyl compounds of the formula

R'—CO—R

in which R and R' have the above meaning, in noncompartmented cells, wherein a mixture which contains from 5 to 75% by weight of the carbonyl compound, from 5 to 90% by weight of the alcohol corresponding to the carbonyl compound, of the formula



$$\underset{R'}{R\text{-}CH\text{-}OH}$$

from 0.1 to 3% by weight of the quaternary ammonium salt and from 0 to 3% by weight of water is used for the electrolysis.

2. A process as claimed in claim **1**, wherein the mixture used for the electrolysis in addition contains from 1 to 30% by weight of dioxan and/or from 5 to 70% by weight of methanol.

3. A process as claimed in claim **1**, wherein acetone is used as the carbonyl compound.

* * * * *