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ELECTROREDUCTION OF 2,2,5,5-TETRAMETHYLCYCLOHEXANE-1,3-DIONE ON MERCURY

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Abstract—The electroreduction of the 1,3-diketone I on a mercury electrode in 2-propanol/water solution was investigated. Current-potential curves at different concentrations were measured and preparative electrolyses at different constant potentials were carried out. The main products formed were isolated and identified as the pinacol II and the keto alcohol III. The ratio of the yields keto alcohol III/pinacol II was found to be potential dependent. A possible mechanism for the formation of the products, accounting for the experimental data, is presented and discussed.

INTRODUCTION

1,3-DIKETONES represent an interesting group of compounds for the study of reduction reactions. Intramolecular interaction between the two CO functions has been detected during electrochemical,[1] Li/NH_3,[2] and Clemmensen[3–5] reductions. Some polarographic measurements[6–10] and a few preparative electrolyses[1, 8, 11, 12] of such compounds have been previously reported.

The purpose of this work was to investigate the electrochemical behaviour of a representative 2,2-disubstituted-1,3-diketone in a protic medium; to identify the products obtained and to rationalize their formation.

RESULTS AND DISCUSSION

Current/potential curves for several concentrations of 2,2,5,5-tetramethylcyclohexane-1,3-dione(I) in 2-propanol containing 7% water (0·5 M tetraethylammonium-*p*-toluenesulfonate (Et_4Np-T.S.) as an electrolyte) are presented in Fig 1. The current/potential curves become independent of the concentration in solutions above 0·15 M in I, probably due to saturation of the electrode surface by adsorbed reactant molecules.[13]

A series of preparative experiments was carried out at different constant current-densities. The potential was measured and found to stay constant throughout each electrolysis. Representative results are summarized in Table 1.

The major products were identified as the pinacol II* and the keto-alcohol III. These were accompanied by a considerable number of mostly unidentified minor products (as shown by GLC evidence). The total amount of these minor products increased as higher potentials were employed in the electrolyses. Possibly these minor products might have been formed by further reductions of III and IV involving charge transfer. The observation, that at potentials more negative than 2·55 Volts (SCE) substantial amounts of 2,2,5,5-tetramethylcyclohexane-1,3-diol were formed, tends to support such an explanation.

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* NMR data suggests a mixture of d, l and meso stereoisomers (See Experimental for discussion).

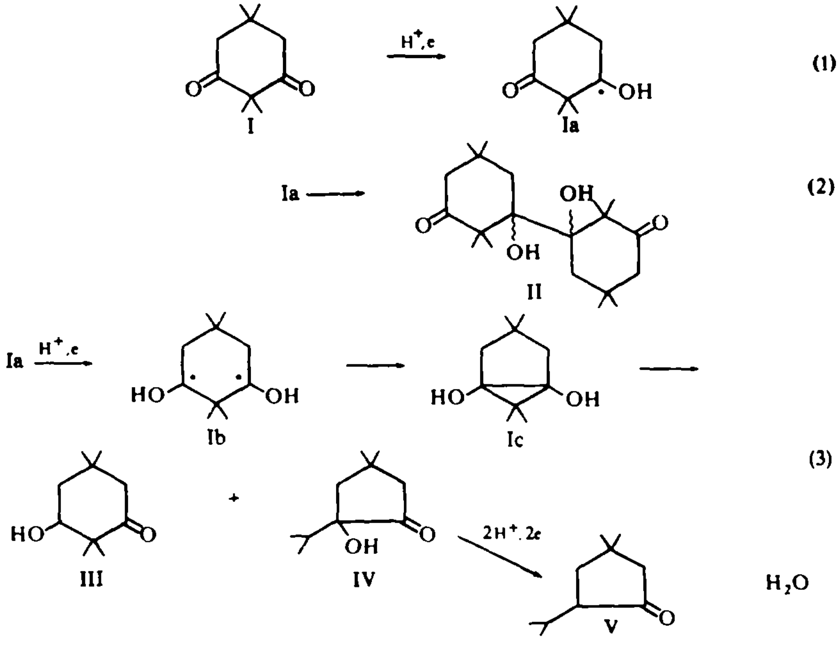
TABLE 1. RESULTS OF PREPARATIVE ELECTROLYSES OF I (0·1 M) IN 2-PROPANOL CONTAINING 7% OF WATER AND 0·5 M Et_4Np-T.S.

Current density (mA cm^{-2})	Potential (Volts SCE)	Time (hr.)	Composition of reaction mixture: Reactant I (%)	Keto-alcohol III (%)	Pinacol II (%)	Complex mixture of minor products (%)
1·28	−2·06	6	72	3	22	3
2·56	−2·12	3	62	4	27	7
5·13	−2·16	1·50	59	5	28	8
10·26	−2·55	0·75	54	17	19	10

With increasing current-density (and consequently of cathodic potential), the overall Faradaic yield of the reaction increases, and so does also the ratio of products III to II formed.* This latter fact can be explained by assuming that both II and III are formed from the same intermediate, namely from the radical Ia, which results from the first electron transfer (Eq. 1). The formation of III from the radical Ia is a charge transfer process (Eq. 3) and its rate is potential dependent, while the formation of II by dimerization of Ia (Eq. 2) is a chemical surface reaction occurring at a rate which is independent of potential.

Two additional compounds IV and V were detected in trace amounts in the reaction mixtures of the electrolyses conducted at high negative potentials. These were also the mixtures which were relatively rich in the ketoalcohol III.

The above observations may be accounted for by the following mechanism which is suggested for the electroreduction of I:



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* Investigation of samples taken at intervals of 30 min proved that the ratio III/II was constant for a given potential and did not depend on the time of electrolysis.

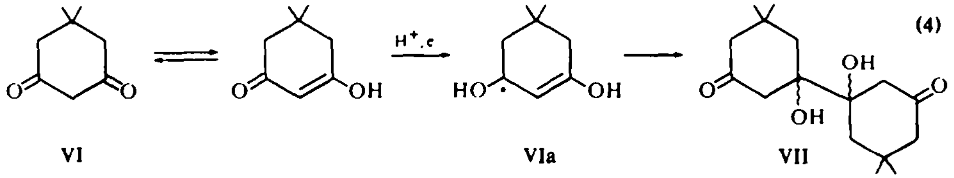
In the first step, I adds a proton and an electron to form the radical Ia, which has been observed[13] to possess a certain "homoallylic"-type stabilization. This radical Ia can undergo either of two competing reactions: dimerization to the pinacol II (Eq. 2), or further reduction to the diradical Ib (Eq. 3).

The diradical Ib isomerizes through ring closure to the cyclopropane-diol Ic which being unstable under the conditions employed[14, 15] is cleaved by two alternative modes leading to the formation of III and IV, respectively. Subsequent reduction of IV may result in the formation of compound V.

Of the two reaction paths available for the radical Ia, only Eq. (3) involves a charge transfer. As pointed out above, this may explain the higher relative yields of III at more negative electrode potentials (Table 1).

The mechanism suggested above is consistent with previously published work[1] in which cyclopropanediol derivatives were obtained from the electroreduction of 1,3-diketones in an aprotic medium.

It is interesting to compare the present results with the electrochemical behaviour of dimedone VI under identical conditions.[11–13] The only product which could be detected[11, 12] in the electroreduction of VI was the corresponding pinacol VII, which was assumed to arise by dimerization of a first formed radical intermediate VIa (analogous to Ia) according to the equation:

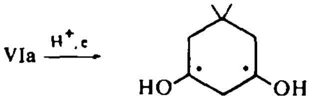


VI VIa VII

(4)

The increased stabilization of the allylic-type radical VIa, as compared with Ia, accounts for the fact that the initial reduction potential E_i[*] of VI is lower than that of I by 0·29 Volts.[13] This difference of 0·29 Volts is equivalent to 6·7 kcal/mole.

The relative stability of the radical VIa may also explain why monomeric reduction products analogous to III, IV and V, are apparently not formed in the reduction of VI, if one assumes that these products are formed via a diradical, such as Ib (Eq. 3).



VIb

(5)

In a diradical VIb, which might form from VIa, the allylic stabilization of the latter will be lost. Similarly, the "homoallylic type" stabilization of Ia is lost once it is converted to Ib. Thus, the two diradicals Ib and VIb should possess approximately equal energies. Consequently, the energy difference between Ib and its "parent" radical Ia will be relatively small as compared with the difference between VIb and

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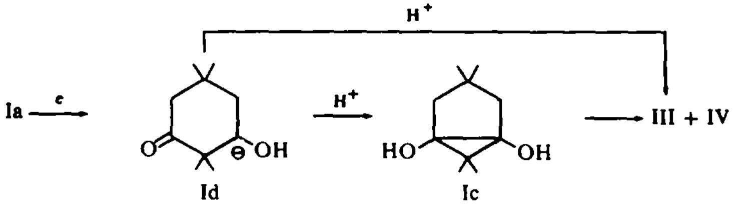
[*] The initial reduction potential E_i has been defined as the value of the potential obtained by extrapolating the current/potential curve measured at high concentration (where it becomes independent of concentration) to zero current density.

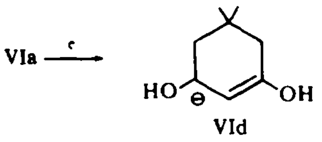
its "parent" VIa (whose energy is considerably lower than that of Ia). In other words, more energy is required for the reaction of Eq. 5 than for the reaction of Eq. 3, in agreement with the fact that (under the experimental conditions reported up to a potential of −2·4 Volts (SCE)[12]) no products which might arise from the diradical VIb could be detected in reaction mixtures from the electrolyses of VI.

On the other hand, this last-mentioned observation would be inconsistent with an alternative mechanism which might be suggested instead of Eq. (3), namely an anion mechanism of the type:



(6)

According to a similar mechanism, VIa may give rise to the anion VId as follows:



(7)

It can be seen that the anions Id and VId should exhibit essentially the same stabilization as the radicals Ia and VIa, respectively, and should be formed from the latter with essentially equal ease. Moreover,the overall energy of formation of VId from VI should be considerably lower than that of Id from I. So there would be no apparent reason why monomeric products of VI should not be obtained by a reaction analogous to Eq. (6).

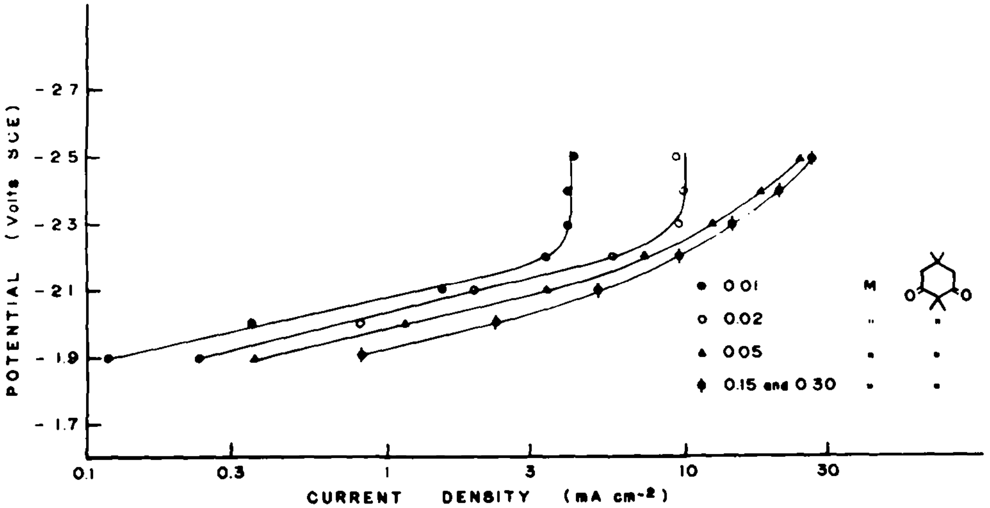


FIG 1. Current/potential curves for the reduction of 2,2,5,5-tetramethylcyclohexane-1,3-dione(I) in 2-propanol 7% water (0·5 M Et_4Np–T.S.)

The fact that such products were not detected leads to the conclusion that the products III and IV are formed from I via a diradical mechanism (Eq. 3) and not through an anion intermediate (Eq. 6).

EXPERIMENTAL

Materials and purification methods. Mercury "Merck" (G.R. and for polarography) was filtered and redistilled before use. 2-propanol was purified by distillation over $NaBH_4$ and Mg under N_2.[16] Double distilled water was used and the N_2 was purified from traces of organic and reducible substances. Tetraethylammonium-*p*-toluenesulfonate (Et_4Np–T.S.)[17] was prepared from ethyl-*p*-toluenesulfonate and triethylamine, recrystallized from EtOH/ether and dried under vacuum over P_2O_5. Compound VI "Fluka" puriss was recrystallized from MeOH/water and I[18] was obtained by methylation of VI and recrystallization from light petroleum.

Electrical measurements and preparative electrolyses. A dropping mercury electrode from a fine polarographic capillary served as the working electrode. The drops were knocked off every 0·24 sec by means of an electromechanical timing device ("Metrohm", A. G. Herisau, Schweiz, E-354 polarographic stand. The maximum drop-size was calculated by weighing all the drops collected in 10 min and assuming a hemispherical shape. A commercial saturated calomel electrode ("Radiometer" type K 401) was used as a reference and a platinized Pt foil served as the counter electrode. All potentials reported are *vs* this reference electrode.

Current/potential measurements were performed potentiostatically using an "Elron" model CHP-1 potentiostat. The potential was varied linearly with time, at a rate of 1 mV/sec by means of a function generator ("Elron" model CHF-1). Current/potential curves were plotted on an X–Y recorder ("Moseley" model 7030 AM). Maximum currents were measured at each potential, corresponding to maximum drop size, just before the drop was knocked off. No effect due to limited response time of the X–Y recorder could be detected on an oscilloscope. N_2 was bubbled through the soln before each measurement and over it during the measurement. Measurements and preparative electrolyses were carried out in 0·5 M Et_4Np–T.S. in 2-propanol and 7% water. Preparative electrolyses were performed galvanostatically with the aid of a high output voltage galvanostat (± 100 V)* in large cells with a mercury pool (19·5 cm^2) cathode. The counter electrode (platinized Pt foil) was enclosed in an alundum tube dipping into the soln and the reference electrode was brought within 1 mm from the surface of the mercury pool. The substance to be reduced was introduced only into the cathode compartment and N_2 was bubbled during electrolysis. After a preparative electrolysis was carried out the solvent was evaporated under vacuum, saturated NaCl aq was added and the mixture was repeatedly extracted with ether. The ether fraction was washed with saturated NaCl aq, dried and the solvent was removed.

Separation and identification of products. IR spectra were recorded on a "Perkin–Elmer" infrared model 337. NMR spectra were recorded on a "Varian HA-100" and reported in δ ppm units. Mass spectra were measured on a "Atlas CH_4" instrument. Mol wt was determined by the isopiestic method (solvent, ethyl acetate 40°) on a "Hitachi Perkin–Elmer" molecular weight apparatus. Gas chromatography was performed on "Aerograph 90P" ("Varian") on the following columns:

SE-30 on 100/120 Var-A-part 30 (5′ × ¼″) and 1% carbowax 20 M on chromosorb W 30/60 HMDS (20′ × ⅜″).

The results of some representative preparative experiments are summarized in Table 1 (*cf* Results and Discussion).

The white crystalline product obtained after "work up" of the preparative electrolyses was chromatographed on acid washed alumina ("Fluka" act. II). It consisted of two main products: (a) *the keto alcohol* III m.p. 51–52° (corr.) (lit[19] 51–52°) which was compared (IR, NMR, GLC) with an authentic sample obtained by catalytic hydrogenation of I;[19] (b) *the pinacol* II m.p. (MeOH) 78° (corr.) (Found: C, 70·82; H, 9·95; $C_{20}H_{34}O_4$ requires: C, 70·97; H, 10·13%); IR (KBr): 3430 (OH), 1690 and 1720 cm^{-1} (C=O); NMR ($CDCl_3$): 0·96 s (3H), 1·01 s (3H), 1·08 s (6H), 1·10 s (3H), 1·13 s (3H), 1·23 s (3H), 1·26 s (3H); mass spectrum *m/e*: 336 (M-2), 169 (M/2). Molecular weight 341.

As judged from its NMR spectrum the pinacol II seems to be a mixture of the d, l and meso stereo-

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* Designed by Mr. N. Tshernikovski in this laboratory

isomers.* It has 7 Me singlets (one of them corresponding to 6H). The meso and d, l stereoisomers have a symmetrical structure and should give at most 4 Me singlets, unless H-bonding disturbs the molecular symmetry. This last possibility was checked by recording the NMR spectrum at high temps (up to 200° in hexachlorobutadiene). No coalescence of the Me peaks could be detected. Attempts to separate the two stereoisomers (assuming that II is a mixture) by TLC with different eluents, GLC and chromatography on different columns were unsuccessful.

In the reduction mixtures of relatively high content (more than 15%) of III traces of compounds IV and V could be detected by GLC. They had identical retention times (on the two GLC columns used) as authentic IV and V isolated from the Clemmensen reduction of I (cf. next paragraph). Moreover, when pure IV and V were added to the electrochemically obtained mixture, the respective peaks on the chromatogram proportionally increased.

Clemmensen reduction of I. 0·012 moles of I were dissolved in 20 ml 4 M HCl in 75% aqueous MeOH. 8 g amalgamated Zn were added and the mixture was stirred and refluxed for 15 min. After cooling, the mixture was extracted with ether. The ether extract was washed with 10% Na_2CO_3aq then with saturated NaClaq, dried and the solvent removed. The residue was chromatographed on acid washed alumina ("Fluka" act. II) and it consisted of 15% *rearranged keto alcohol* IV m.p. (pentane) 59° (corr.); IR (neat) 3460 (OH) 1740 cm^{-1} (C=O); NMR 0·82 d (3H), 1·12 s (3H), 1·27 d (3H). (Found: 70·66; H, 10·60 ($C_{10}H_{18}O_2$ requires: C, 70·54, H, 10·66%), DNP of IV m.p. (MeOH) 194°. Upon formation of the DNP one molecule of water is lost therefore its analysis fits the formula $C_{16}H_{20}N_4O_4$. (Found: C, 57·71; H, 6·02 (mol formula requires: C, 57·82; H, 6·07%).

Cyclopentanone V[19]; its DNP has m.p. (MeOH) 144°, lit.[19] 145°. (Found: C, 57·34; H, 6·72 ($C_{10}H_{18}O$ requires: C, 57·47; H, 6·63%). In addition, a mixture (8·8%) of low polar compounds which did not have a CO function, 3% of III and the remaining starting compound were isolated.

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* The NMR peaks seem to show a 1:1 ratio but positive identification of the peaks for the unknown compounds could not be made.