The Electrochemical Reduction of 1,3-Diphenyl-1,3-propanedione[1]

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Electrochemical reduction of 1,3-diphenyl-1,3-propanedione (1) in 50% ethanol–water at mercury cathodes produces several products depending on solution pH and the potential of the cathode. The first process is the one-electron reductive dimerization to the pinacol, 1,4-dibenzoyl-2,3-diphenyl-2,3-butanediol (2). At more cathodic potentials a two-electron process was identified. The electrolysis product was a mixture which was not fully characterized. In alkaline solutions a four-electron process occurs and the product is a mixture of the two isomers of 1,3-diphenyl-1,3-propanediol (6). The effects of chemical reactions following the electrochemical reduction and the electrochemical behavior of the isolated products are discussed.

In the many years since the development of polarography, the selective and direct electrochemical reactions inferred from dropping mercury electrode data have tempted the organic chemist to scale-up the microelectrolysis conditions of polarography to macro-controlled-potential reductions at mercury-pool cathodes and thus to provide general yet selective electrosynthetic procedures. Unfortunately polarographic data do not always provide an adequate basis upon which to develop such synthetic procedures.

Two of the reasons for this are (1) that the time scale of polarography is controlled by the lifetime of a single mercury drop (a few seconds) while the time scale of a synthetic electroreduction ranges from a few minutes to a few hours (thus undesirable chemical reactions following the electrochemical reaction can become dominant in the large-scale electrolysis even though they are too slow to affect the polarographic data); and (2) though the number of electrons consumed per reacting molecule (*n* value) can be obtained from polarography and controlled-potential coulometry, several discrete products may often be postulated for a reaction of given *n* value. Thus systematic product analysis must be coupled with the usual polarographic and controlled-potential coulometric studies in order to develop useful electrochemical methods of synthesis.

Quite logically, the carbonyl function has been the subject of extensive electrochemical investigation,[2] but, nonetheless, ambiguities remain. In particular the suggested reaction pathways for most of the electrochemical reductions of carbonyl compounds have neither the supporting evidence of coulometrically obtained *n* values nor the corroboration of identified products. In the case of monofunctional carbonyl compounds the reactions are simple because reduction in protic systems leads only to pinacol formation, carbinol formation or exhaustive reduction to the corresponding alkane with accompanying *n* values of 1, 2, and 4, respectively. The presence of one additional functional group, however, makes any prediction of product identity rather tenuous.

β-Diketones are a particularly interesting subject for electrochemical study, not only because of the numerous possibilities for reduction pathways, but also because of the large number of such compounds readily available and hence of potential synthetic use. Previous studies of the electrochemical reduction of β-diketones have been limited to surveys of polarographic behavior.[3,4] These included a study of 1,3-diphenyl-1,3-propanedione (1), a typical symmetrical β-diketone, which was reported to give as many as three different waves under various conditions, thus suggesting at least three different reductive products.[3b] A more complete investigation of the electrochemical reduction of β-diketone 1 is the subject of this communication.

Polarography.—Polarographic data for the reduction of 1 are summarized in Table I.[5] A plot of half-wave potential *vs.* pH produces a curve lying from 20 to 100 mv to the anodic side of a similar plot of the data of Philp, Flurry, and Day.[3a] Part of this discrepancy may stem from the different buffer systems used in the two studies (see data for borate and carbonate buffers (Table I), but a significant difference still exists. The 0.2–0.3-v discrepancy between the present data and the early work of Pasternak[3b] remains an enigma. The half-wave potentials of the first two waves vary approximately 59 mv per pH unit. For monofunctional phenyl ketones the first wave behaves similarly but the second wave is pH independent[6] suggesting that the second wave of 1 is of a different nature than the second wave of a monoketone.

The third wave reported by Pasternak[3b] in alkaline solutions was just discernible in the borate and carbonate buffers. In 0.10 *M* sodium hydroxide it appears as a separate wave at −1.75 v *vs.* saturated calomel electrode (sce) (aqueous) and in tetramethylammonium hydroxide it has fused with the first two to form one, drawn-out, composite wave.

Plots of diffusion current *vs.* the square root of effective mercury column height for the first wave were linear and passed through the origin in all solutions. These observations coupled with the reasonably constant diffusion current constants in the concentration range 0.00018 to 0.003 *M* are indicative of a diffusion-controlled process. The general decrease in

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[1] This work was supported in part by the Wisconsin Alumni Research Foundation. Presented at 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

[2] (a) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1955, Chapter 29; (b) G. W. C. Milner, "The Principles and Applications of Polarography and Other Electroanalytical Processes," Longmans, Green and Co., London, 1957, Chapter 22.

[3] (a) R. H. Philp, R. L. Flurry, and R. A. Day, *J. Electrochem. Soc.*, **111**, 328 (1964); (b) R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1948); (c) G. Semerano and A. Chisini, *Gazz. Chim. Ital.*, **66**, 504 (1936).

[4] (a) I. A. Korshunov, A. S. Kirillova, and Z. B. Kuznetsova, *Zh. Fiz. Khim.*, **24**, 551 (1958); (b) S. I. Vityaeva and A. L. Markman, *Trudy Sredneaz. Politekh. Inst.*, **2**, 17 (1957); (c) W. Rogers, Jr., and S. M. Kipnes, *Anal. Chem.*, **27**, 1916 (1955); (d) H. Adkins and F. W. Cox, *J. Am. Chem. Soc.*, **60**, 1151 (1938); (e) I. Tachi, *Mem. Coll. Agr. Kyoto Univ. Chem. Ser.*, **42**, 27 (1938).

[5] Half-wave potentials ($E_{1/2}$) have been corrected for *iR* drop.

[6] P. J. Elving and J. T. Leone, *J. Am. Chem. Soc.*, **80**, 1021 (1958).

TABLE I

POLAROGRAPHY OF 1,3-DIPHENYL-1,3-PROPANEDIONE

pH	Wave 1		Wave 2		Wave 3	
	$E_{1/2}$[a,b]	I[b,c]	$E_{1/2}$[a,b]	I[b,c]	$E_{1/2}$[a,b]	I[b,c]
1.4 (HCl)	-0.85 ± 0.00	1.47 ± 0.03				
4.2[d] (citrate)	-1.10 ± 0.01	1.20 ± 0.02	-1.35 ± 0.01	*Ca.* 1.6		
6.1[d] (citrate)	-1.22 ± 0.01	1.28 ± 0.09	-1.40 ± 0.01	1.53 ± 0.05		
9.9[d] (borate)	-1.40 ± 0.01	1.13 ± 0.02	-1.60 ± 0.01	0.96 ± 0.04	*Ca.* -1.85	*Ca.* 2.5
10.0 (carbonate)	-1.42 ± 0.00	0.98 ± 0.01	-1.61 ± 0.00	0.76 ± 0.02	*Ca.* -1.85	
13.6 (NaOH)	-1.54	0.8	-1.62	0.7	-1.75	1.6
13.5 [$(CH_3)_4NOH$]					(-1.54 ± 0.02)[e]	(3.38 ± 0.10)[e]

[a] Half-wave potentials are *vs.* sce (aqueous), volts. [b] Typically an average value from measurements at three–four concentrations between 0.00018 and 0.003 *M*. Deviation given is average deviation. [c] I = diffusion current constant = $i_d/m^{2/3}t^{1/6}C$. Units: μa sec$^{1/2}$ mg$^{-2/3}$ mM^{-3}. [d] 0.01% gelatin, maximum suppressor. [e] Composite of all three waves. Two waves of equal height were just discernible at the highest concentration, 0.003 *M*.

diffusion current constant at a pH greater than 9 is partially due to the fact that an increasing fraction of **1** exists as the more slowly diffusing enolate anion. Finally it should be noted that substitution of the diffusion currents in the Ilkovic equation produces reasonable values of the diffusion coefficient ($3-6 \times 10^{-6}$ cm^2/sec) if an n value of 1 is assumed, an assumption for which more conclusive evidence will be presented below.

For the second wave plots of diffusion current *vs.* the square root of the effective mercury column height deviate significantly from linearity at pH 6.1 and even more so at pH 4.2. The ratio of the diffusion current of the second wave to that of the first approaches 1 at short drop times (high $h^{1/2}$) whereas at long drop times (low $h^{1/2}$) the ratio is as great as 1.5 at pH 6.1 and 1.7 at pH 4.2 (h_{eff} = 20 cm). This is the behavior expected in an ece mechanism[7,8] in which the product of the electrochemical reaction reacts further to form other electroactive materials. In the borate and carbonate buffers, however, linear plots of current *vs.* square root of column height are obtained. This strongly suggests that in acidic media the reduction product of the second wave is converted to a new compound which undergoes further reduction, whereas in basic media the initially formed product is stable.

The ratio of diffusion currents of the first two waves is difficult to establish since the waves are quite close to one another on the potential axis. Nevertheless, a total two-electron process at the second wave is supported by the approximate ratio of one obtained in alkaline solutions and the approach to a ratio of one at short drop times in acid solutions.

The third wave, when discernible, approximately equals the total magnitude of the first two, indicating a total four-electron process. This conclusion is also supported by the fact that the total diffusion current in sodium hydroxide and tetramethylammonium hydroxide is about four times the diffusion current for the first wave.

TABLE II

CONTROLLED-POTENTIAL COULOMETRY OF 1,3-DIPHENYL-1,3-PROPANEDIONE

pH	Quantity, mg	E[a]	n[b]
		Wave 1	
1.4	22.4	-1.00	. . .[c]
	67.3	-1.00	. . .[c,d]
4.2	23.2	-1.25	1.55
	38.5	-1.20	1.19
	25.3	-1.15	1.01
9.9	57.6	-1.50	1.13[e]
10.0	66.4	-1.50	1.17
		Wave 2	
4.2	68.3	-1.50	. . .[c]
6.1	68.0	-1.55	>2[c]
9.9	54.1	-1.75	2.01[e]
10.0	57.0	-1.75	1.89
13.6	74.3	-1.70	1.93
		Wave 3	
13.5	30.3	-2.00	4.13[e]

[a] Control potential *vs.* sce (aqueous), volts. [b] Experimental n value. [c] Large residual current. [d] At 8°. [e] No precipitate.

Controlled-Potential Coulometry.—Table II summarizes data obtained for the controlled-potential reduction of **1**. Electrolyses at potentials on the plateau of the first polarographic wave were carried out in solutions of pH 1.4, 4.2, 9.9, and 10.0. In the most acidic solution, a yellow color developed as the electrolysis proceeded, the residual current approached 15–30% of the initial current, and n values calculated by any procedure exceeded 1. This behavior persisted at low temperatures though the yellow color was less intense. In view of the anticipated formation of hydroxylic products, acid-catalyzed dehydration can be expected, a process undoubtedly enhanced by the formation of conjugated double bonds. Compounds of this type are apt to be more easily reduced[3a] than the starting material and if formed would contribute to the current at the control potential. The dehydration reaction is fast enough to complicate the controlled-potential reduction which requires about 1 hr, but it is not fast enough to cause nonlinearity in the i_d *vs.* $h^{1/2}$ plot under polarographic conditions (time scale 2–10 sec).

In less acidic solutions the dehydration is slow enough that entirely normal controlled-potential behavior is obtained. At pH 4.2, the n value is exactly 1 when the potential is controlled at a value just before the plateau, *i.e.*, at -1.15 v *vs.* sce (aqueous). The current–time curves are exponential and the residual currents are no greater than residual currents obtained with supporting electrolyte alone. Polarograms of the solution after electrolysis are indistinguishable from those of the supporting electrolyte out to the control potential. All of these observations are indicative of the simple, one-electron reduction of **1**. The reduction product separates as a finely divided, white solid as the electrolysis proceeds.

The two waves of a polarogram of **1** in pH 4.2 buffer are not well separated. No true diffusion

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[7] A. C. Testa and W. H. Reinmuth, *Anal. Chem.*, **33**, 1320 (1961).

[8] G. S. Alberts and I. Shain, *ibid.*, **35**, 1859 (1963).

current plateau is observed for the first wave. When controlled-potential reductions were carried out at a potential midway between the half-wave potentials of the two waves, *i.e.*, at -1.20 v *vs.* sce (aqueous), n values of about 1.2 were obtained indicating that some two-electron reduction was taking place. Even higher n values were obtained at more cathodic potentials. These observations indicate that a significant fraction of the current when the control potential is at the top of the first wave is due to the reaction of the second wave. Part of this behavior may be due to uneven potential distribution at the mercury pool cathode.[9]

Analogous situations were encountered in the borate and carbonate buffers in which controlled-potential reductions at the top of the first wave produced n values of 1.13 and 1.17, respectively. In the borate buffer the product did not precipitate during electrolysis. Soluble borate complexes were formed.[10]

Reductions at the second wave were not successful at pH 4.2 and 6.1. Again the wave is not well separated from the preceding wave and there is significant decomposition of the reaction product.

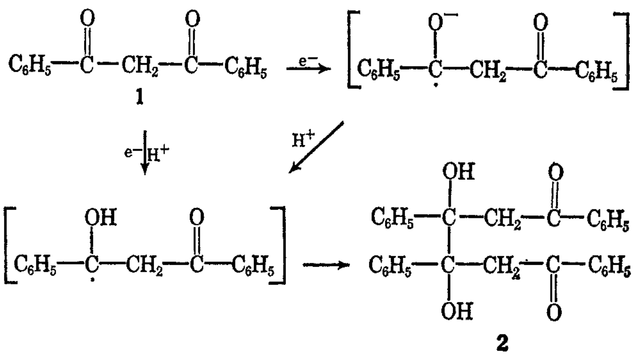
In borate and carbonate buffers, however, more normal controlled-potential reductions were observed. Current–time curves were exponential and residual currents were normal. In this case it was found to be best to electrolyze at the foot of the third wave in order to obtain n values of 2. In the carbonate buffer the product begins precipitating after the first few minutes of electrolysis, while in the borate buffer no precipitate is formed since the product is again complexed by borate.

One electrolysis was performed in 0.1 *M* sodium hydroxide yielding an n value of 1.93. The behavior in this solution was very similar to that observed in the carbonate buffer.

A reduction on the third wave was performed in 0.1 *M* tetramethylammonium hydroxide. The n value was 4.13 and the electrolysis product remained in solution.

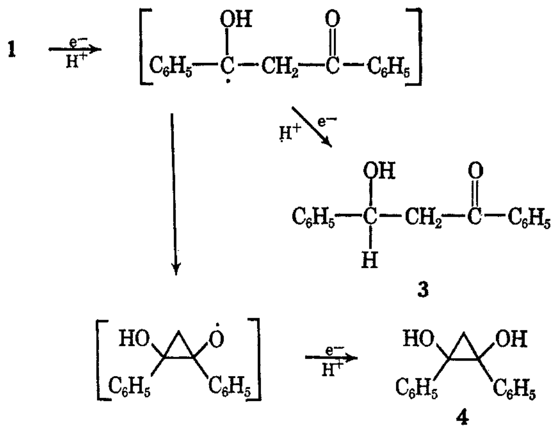
The above polarographic and coulometric results imply formation of three different reduction products with the consumption of one, two, and four electrons, respectively, per molecule of starting diketone. Any process involving but a single electron necessitates formulation of an intermediate radical anion which can be protonated to a neutral, free-radical species. Such a process might be expected to lead to a variety of products for an intermediate free radical could yield stable products *via* numerous pathways and not necessarily react selectively. At least three types of products could arise from the free-radical through (1) dimerization, (2) hydrogen abstraction from the solvent, and (3) combination with the mercury electrode.[11] In this case the second process is not expected to be energetically favorable and no evidence supporting the third process has been found. The first process is depicted in Scheme I. The concerted addition of an electron and a proton (or the reduction of a protonated species) is supported by the marked pH dependence of the first polarographic wave.[6]

SCHEME I



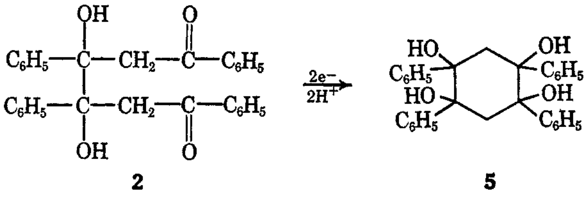
A two-electron reduction of the substrate, accompanied by or followed by the addition of two protons, suggests two possible products (Scheme II).

SCHEME II



The formation of cyclopropanediol species is not unprecedented. The data of Cusack and Davis[12] strongly suggest the general intermediacy of such compounds in the Clemmensen reduction of β-diketones. The strongly acidic nature of Clemmensen conditions would then induce a pinacol rearrangement and dehydration to give an α,β-unsaturated ketone, subsequently reducible to the saturated ketone. Under the considerably milder conditions of the electrochemical reduction, a cyclopropanediol might be stable to rearrangement and further reduction.

In addition to two-electron reductions of the substrate **1**, the second wave could be the result of a two-electron reduction of any dimeric product formed at the first wave, such as the pinacol **2**. Such a process could yield a cyclic tetrol.



A simple, four-electron reduction of **1** would be expected to give the monomeric diol, **6**. Diol **6** as well

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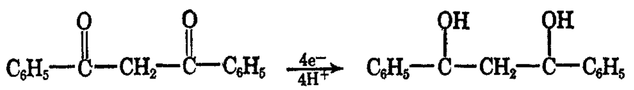
(9) J. E. Harrar and I. Shain, *Anal. Chem.*, **38**, 1148 (1966).

(10) J. Dale, *J. Chem. Soc.*, 910 (1961).

(11) *Cf.* M. D. Morris, P. S. McKinney, and E. C. Woodbury, *J. Electroanal. Chem.*, **10**, 85 (1965), and references cited for examples of Hg inclusion during the reduction of organic compounds.

(12) N. J. Cusack and B. R. Davis, *J. Org. Chem.*, **30**, 2062 (1965).



$$C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[4H^+]{4e^-} C_6H_5-\overset{OH}{\overset{|}{C}}-CH_2-\overset{OH}{\overset{|}{C}}-C_6H_5$$

1 6

as other products could also arise from further reduction of two-electron reductions products such as **3**, **4**, or **5**. However, the two-electron reduction product was found to be not electrochemically reducible.

Preparative-Scale Electrolyses.—The pH 4.2 citrate buffer was chosen for preparation of the product of the first wave. The ether-soluble fraction of the product was found to be **2**.

Electrolysis on the second wave produced a mixture of materials thought to be mainly the isomers of **5**. Electrolysis on the third wave was carried out in 0.1 *M* tetramethylammonium hydroxide and both isomers of **6** were found as products.

These data indicate that **1** is reduced at the first wave to **2** requiring one electron per molecule of **1** and that **2** is reduced at the second wave in a process requiring one additional electron per starting monomer (**1**) or two electrons per molecule of **2**. Since solutions containing either **2** or the product(s) of reduction at the second wave show no polarographic wave at the third wave of **1**, this third wave cannot be due to the reduction of either intermediate but rather is due to the more extensive reduction of **1**, the four-electron reduction to **6**.

In conclusion it can be seen that although the dimeric pinacol **2** and the monomeric diol **6** were found to be products of reduction at the first and third waves, respectively, no monomeric two-electron product was found. It seems that dimeric reduction products are favored under the electrochemical conditions and the electrochemical preparation of such dimeric products may be one of the unique advantages of electrochemical syntheses. The problem of stereochemistry of the products, dimeric and monomeric, has yet to be examined. Unfortunately it appears that none of the reductions was stereochemically specific, although the precise ratio of *dl* and *meso* products was not determined.

Experimental Section[13]

Apparatus.—A Leeds and Northrup Electro-Chemograph and standard H cell were used in polarographic measurements. Diffusion current measurements were made with the damping set at "galvanometer equivalent." The average currents were corrected for residual currents which were measured from polarograms of the various supporting electrolytes.

A mercury stand tube with automatic *m* determiner[14] was used. The capillary used had an *m* value of 1.58 mg/sec at an h_{eff} value of 49.4 cm. Drop times varied from 4.4 to 2.6 sec for the range of solutions and potentials used.

The potentiostat was a Wenking Model 61RS (Brinkmann Instruments, Inc., Westbury, N. Y.). Controlled-potential coulometry was carried out at a mercury pool in a cell previously described.[15] (A mercury pool was used instead of the wire electrode shown.) Preparative electrolyses were carried out in a 500-cc reaction kettle (Kimax, No. 33700, Owens-Illinois, Toledo, Ohio). The auxiliary electrode was separated from the catholyte in a medium-porosity sealing tube. The anolyte was 0.5 *M* potassium nitrate in 50% ethanol-water. The reference electrode probe was terminated by a cracked-glass seal.[15] All electrode compartments and gas inlets were inserted through standard taper joints in the top of the reaction kettle. Stirring was effected by a magnetic stirrer.

Current-time curves were recorded with a Sargent Model MR recording potentiometer. Integrations were performed graphically.

Reagents.—The 1,3-diphenyl-1,3-propanedione was Eastman White Label. It was used as received. Vacuum sublimation did not alter the melting point (76–77°). Buffer constituents were of analytical reagent quality except the tetramethylammonium hydroxide which was Eastman White Label. Prepurified nitrogen (99.98%) was used to deaerate solutions. Mercury was triply distilled.

Procedure.—Buffer compositions were as given in Table III. All solutions were 50% ethanol-water. The pH of each buffer was measured using a glass electrode calibrated with standard aqueous buffer systems.

TABLE III

pH	Composition
1.4	0.2 *M* hydrochloric acid
4.2	0.67 *M* sodium chloride 0.27 *M* sodium citrate, monobasic 0.13 *M* sodium citrate, dibasic
6.1	0.10 *M* sodium chloride 0.20 *M* sodium citrate, tribasic 0.10 *M* sodium citrate, dibasic
9.9	0.10 *M* potassium borate 0.10 *M* boric acid
10.0	0.05 *M* sodium carbonate 0.05 *M* sodium bicarbonate
13.5	0.10 *M* tetramethylammonium hydroxide 0.10 *M* tetramethylammonium chloride
13.6	0.10 *M* sodium hydroxide

Preparation of Product at the First Wave.—The reaction kettle electrolysis cell was set up with 500 cc of pH 4.2 catholyte. A solution of 350 mg of **1** in 10 cc of 95% ethanol was added and electrolysis was carried out at −1.15 v *vs.* sce (aqueous). The current fell from about 70 to 8 ma in 2 hr, at which time another 350 mg of **1** was added and electrolysis was continued. This procedure was repeated until 2.1 g of **1** had been added. After 18 hr the total quantity of **1** had been added and the electrolysis current had decreased to less than 1 ma. The electrolysis was terminated, and the catholyte and suspended products were separated from the mercury cathode and set aside for 24 hr. The product was filtered off, washed, vacuum dried, and weighed, giving 2.01 g of crude product. The batchwise addition of **1** was used in order not to exceed the solubility of **1** in 50% ethanol, *ca.* 0.0035 *M*.

The product was extracted twice with refluxing ether for 2 and 12 hr, respectively, resulting in 70% dissolution. After evaporation of the solvent, a white solid was obtained. This was shown by thin layer chromatography to be almost entirely the pinacol **2**.

The product was recrystallized twice from absolute ethanol, giving fine, white crystals of **2**, mp 202–203°. The infrared spectrum of **2** showed $\lambda_{max}^{CH_2Cl_2}$ at 2.82, 2.94, 3.27, 3.33, 6.04, 6.26, 6.72, 6.91, and 9.42 μ. In addition to a parent peak (M^+) at *m/e* 450, the mass spectrum showed very large peaks at *m/e* 225, 105, and 77. *Anal.* Calcd for $C_{30}H_{26}O_4$: C, 79.98; H, 5.82. Found: C, 79.87; H, 5.76.

1,4-Dibenzoyl-2,3-diphenyl-1,3-butadiene.—Compound **2** (100 mg) was dissolved in 50 cc of benzene to which was added 5 mg of *p*-toluenesulfonic acid. The solution was refluxed for 1 hr using a Soxhlet extractor with calcium hydride in the thimble to remove water. The crude product was taken up in methylene chloride, extracted with aqueous sodium carbonate, and dried. After evaporation of solvent 90 mg of product was obtained which was then recrystallized from methanol-methylene chloride, giving yellow needles of 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene, mp 194° (lit.[16] mp 190–191°). The infrared spectrum had $\lambda_{max}^{CH_2Cl_2}$ at 3.22, 6.01, 6.23, 6.39, 6.71, 6.92, 7.26, 8.28, 9.66, and 9.83 μ. The mass spectrum showed a parent peak (M^+) at *m/e* 414 and

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[13] Melting points were determined with a Fisher-Johns apparatus and are uncorrected. Mass spectra were determined on an A.E.I. MS-9 instrument. Infrared spectra were recorded on a Perkin-Elmer Infracord, Model 137. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

[14] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

[15] J. J. Lingane, *J. Electroanal. Chem.*, **1**, 379 (1960).

[16] H. W. Bost and P. S. Bailey, *J. Org. Chem.*, **21**, 803 (1956).

large peaks at *m/e* 309, 105, and 77. *Anal.* Calcd for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35. Found: C, 86.87; H, 5.36.

Attempted Acetonization of 2.—An attempt was made to acetonize the diol in order to assign the *meso* or *dl* structures of the acetonide by nmr.[17] Compound 2 (50 mg) was dissolved in 40 cc of acetone, and 0.5 g of anhydrous cupric sulfate was added. The mixture was refluxed for 4 days. Compound 2 was recovered unchanged.

Preparation of Product at Second Wave.—Electrolyses on the second wave in the borate buffer were attempted. The electrolysis solution was neutralized with hydrochloric acid, precipitating a white, amorphous solid, probably a boric acid ester, which was difficult to characterize.

In a typical electrolysis on the second wave in the carbonate buffer, the precipitated electrolysis product accounted for 83% of the starting material. It was a mixture of materials (mp 145–150°) which showed no significant carbonyl but much hydroxyl absorption in the infrared. The mass spectrum revealed significant amounts of dimeric products. The mixture was very soluble in all common solvents save water, cyclohexane, and alkanes. Separation and characterization of the mixture was complicated by its extreme sensitivity to heat, acids, and dehydrating agents. Of the possible two-electron products the isomers of 1,2,4,5-tetraphenyl-1,2,4,5-cyclohexanetetrol (**5**) seem most likely on the basis of the above evidence. Although the formation of 1,2-diphenyl-1,2-cyclopropanediol (**4**) cannot be excluded by either the infrared or mass spectral data, it seems quite unlikely since a sample of the pinacol **2** from the reduction at the first wave is reduced polarographically with an $E_{1/2}$ value identical with that of the second wave of the substrate **1** (*vide infra*). This, combined with the absence of carbonyl absorption in the infrared, further indicates that the expected monomeric reduction product, the ketol **3**, is not formed, contrary to earlier assumptions.[2,3]

Preparation of Product at Third Wave.—The procedure was identical with that used for electrolysis at the first wave except that 0.1 *M* tetramethylammonium hydroxide (50% ethanol-water) was used as supporting electrolyte and the control potential was −2.0 v *vs.* sce (aqueous). The electrolysis of 2.07 g of **1** was complete in 20 hr.

The electrolysis solution was separated from the mercury cathode, neutralized with hydrochloric acid, and evaporated to half its initial volume. Upon cooling a viscous, yellow oil and some white, crystalline material separated. Most of the yellow oil was physically separated from the white material which weighed 0.98 g after drying. Recrystallization from benzene–Skellysolve B produced 0.49 g of racemic **6**, mp 129–130° (lit.[10] 130°, mmp 129–130°).

The filtrate from the electrolysis solution was extracted three times with ether, the extracts were dried, and the ether was evaporated leaving a colorless oil which crystallized after a few hours producing 0.70 g of solid, mp 85–90°. Recrystallization from benzene–Skellysolve B yielded 0.46 g of material, mp 105–107°.[18] Fractional recrystallizations to constant melting point yielded a first fraction with mp 108°. The melting point of the *meso* form of **6** has been reported as 108–109°.[10] This was verified by preparation of authentic samples of the two isomers of **6** by sodium borohydride reduction of **1**.[10] The infrared spectra were identical with those of the electrolytic products.

Electrochemistry of Intermediates and Related Compounds.—The product of the first wave (**2**) was electroactive at the potential of the second wave of **1**, *i.e.*, the second wave is due to the further reduction of the product of the first wave. The half-wave potential of **2** was -1.35_5 v *vs.* sce (aqueous) at pH 4.2 compared to −1.35 v for the second wave of **1**. In the carbonate buffer the half-wave potential of **2** was -1.59_0 v *vs.* sce (aqueous) compared to −1.61 v for the second wave of **1** (Table I). No wave corresponding to the third wave (−1.85 v) was seen with **2**.

When **2** was generated in solution by electrolysis at the first wave in the borate buffer (Table II), the electrolysis solution had a polarographic wave at −1.62 v, very close to the half-wave potential of the second wave of **1** in this medium. Again the third wave was absent.

The product from the dehydration of **2**, 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene, was very easily reduced in a quasi-reversible process as shown by cyclic voltammetry in 0.1 *M* perchloric acid in 95% ethanol [$E_{p/2} = -0.1$ v *vs.* sce (aqueous)]. This behavior is consonant with that of other conjugated diones.[3a] Thus if **2**, which is initially formed during electrolysis on the first wave in 0.2 *M* hydrochloric acid (Table II), dehydrates to the above product, the product would be reduced at the control potential (−1.0 v) and would enhance the current during electrolysis, in accord with experimental observations.

Registry No.—**1**, 120-46-7; **2**, 10562-14-8; **6**, 5355-61-3; 1,4-dibenzoyl-2,3-diphenyl-1,3-butadiene, 10562-16-0.

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The Keto–Enol Equilibrium in 1,3-Cyclohexanediones

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The ultraviolet and nmr spectra of dimedone (I) and 1,3-cyclohexanedione (II) were measured in different solvents at various concentrations. In cyclohexane and chloroform solutions, at very high dilutions, the keto forms of I and II exist in equilibrium with the respective monomeric enol forms. With gradual increase of the concentrations, the dimeric enol form becomes dominant, and at still higher concentrations higher degrees of association of the enol form are observed. The proton and ^{17}O nmr measurements of dimedone (I) at room temperature point to a fast intermolecular hydrogen transfer in the enol form, and to a rapid interconversion of the two conformers Ia and Ib. Lowering of the temperature results in slower interconversion of the two conformers. The activation energy for this process was calculated to be 4.1 ± 0.5 kcal/mole.

The high degree of enolization of acyclic β-diketones has been attributed,[1] among other factors, to stabilization of the enol form by internal hydrogen bonding, hence also the strong solvent dependence of the keto-enol equilibria in these compounds. In the enols of 1,3-cyclohexanediones such internal hydrogen bonding is sterically impossible; nevertheless, these diketones are predominantly enolic. In solvents serving as hydrogen acceptors for hydrogen bonds "nucleophilic" solvents, the enol forms may be stabilized by hydrogen bonding with the solvent.[2] In solvents uncapable of accepting hydrogens, the comparatively high enol content was explained by assuming a dimeric enol form held together by hydrogen bonds.[2] Recently, however, a monomeric enol form was postulated as

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