Tetrahedron, 1959, Vol. 5, pp. 293 to 304. Pergamon Press Ltd. Printed in Northern Ireland

ANODIC REDUCTIONS—V*

THE REDUCTION OF DIKETONES BY UNIPOSITIVE MAGNESIUM ANODICALLY GENERATED

WILLIAM D. HOFFMAN, WILLIAM E. MCEWEN and JACOB KLEINBERG
Department of Chemistry, University of Kansas, Lawrence, Kansas

(*Received* 18 *August* 1958)

Abstract—A series of diketones of the general formula $C_6H_5CO(CH_2)nCOC_6H_5$ has been prepared and subjected to "anodic reduction" in sodium iodide-pyridine solution between magnesium electrodes. In every case hydrolysis of the anolyte following electrolysis yielded a 1:2-diol as the reduction product as evidenced by titration with standard lead tetraacetate solution. The diketones, 1:3-dibenzoylpropane ($n = 3$) and 1:4-dibenzoylbutane ($n = 4$), gave *cis*-1:2-diphenyl*cyclo*pentane-1:2-diol and *cis*-1:2-diphenyl*cyclo*hexane-1:2-diol, respectively. On the assumption that the other diketones also gave cyclic 1:2-diols, there is a striking correlation between the initial mean valence number (V_i) of the magnesium entering solution from the anode and the size of the ring; the lowest V_i values were obtained in those instances where the diketones originally in solution gave the most stable cyclic diols. Interpretations are offered for these results and for corrosion phenomena observed.

A SUBSTANTIAL amount of evidence has been accumulated which indicates that on anodic oxidation in aqueous salt solutions magnesium enters solution at least in part in the unipositive state.[1–3] The latter species has not been isolated in the form of a compound, but is converted rapidly to the dipositive cation as a result of oxidation by the solvent, reducible solutes (e.g. $AgNO_3$, $KMnO_4$), or electrochemically at the anode.

The anodic behavior of magnesium in anhydrous pyridine solutions has also been investigated. This solvent has the advantage over water in that it is reduced only with great difficulty, but is nevertheless a satisfactory electrolytic medium. It has therefore proved to be a useful solvent for study of the effects of organic oxidants on the anodic behavior of magnesium.

In the anodic oxidation of magnesium in sodium iodide-pyridine medium the metal entered solution with an initial mean valence number (V_i) of two.[4] However, in the presence of any one of a number of potential organic oxidants (e.g. benzophenone,[4] 4:4′-dimethylbenzophenone,[5] 2′-methoxy-2:4:6-trimethylbenzophenone,[6] benzil,[5] nitrobenzene,[7] nitrosobenzene,[7] azoxybenzene,[7] and azobenzene[7]) the magnesium went into solution with an initial mean valence number significantly less than two. Under these circumstances a reduction product of the organic additive was isolated from the anolyte, and in a majority of instances the amount of reduction product corresponded essentially quantitatively to that expected from oxidation by the organic additive of the metal from its initial mean valence state to its common

---

* For Part IV see ref. 7.

[1] M. D. Rausch, W. E. McEwen and J. Kleinberg, *Chem. Rev.* **57**, 417 (1957).

[2] J. H. Greenblatt, *J. Electrochem. Soc.* **103**, 539 (1956).

[3] D. V. Kokouliva and B. N. Kabanov, *Dokl. Akad. Nauk SSSR* **112**, 692 (1957).

[4] M. D. Rausch, W. E. McEwen and J. Kleinberg, *J. Amer. Chem. Soc.* **76**, 3622 (1954).

[5] W. E. McEwen, J. Kleinberg, D. L. Burdick, W. D. Hoffman and J. Y. Yang, *J. Amer. Chem. Soc.* **78**, 4587 (1956).

[6] M. D. Rausch, F. D. Popp, W. E. McEwen and J. Kleinberg, *J. Org. Chem.* **21**, 212 (1956).

[7] J. Y. Yang, W. E. McEwen and J. Kleinberg, *J. Amer. Chem. Soc.* **80**, 4300 (1958).

+2 state. It should be emphasized that in only a few of the cases studied was the organic additive itself capable of attacking the massive magnesium anode non-electrolytically. The "anodic reductions" effected in pyridine solution, like those in aqueous solution, are interpreted as being brought about by the action of unipositive magnesium anodically generated.

Although pyridine solutions of the organic additives investigated generally were unreactive toward massive magnesium, primary products of "anodic reduction" were found to be sufficiently reactive to attack the metal. Considerable evidence has been obtained that these primary reduction products are radical-ions and that corrosion proceeds by a chain mechanism in which the radical-ions and unipositive magnesium function as chain carriers.[1,8]

A series of diketones of the general formula $C_6H_5CO(CH_2)nCOC_6H_5$, where n equals two through eight, has now been prepared and subjected to "anodic reduction". The only diketone previously studied was benzil;[5] this was quantitatively reduced to a product which on hydrolysis gave benzoin. On the other hand, simple aromatic ketones, such as benzophenone[4] and 4:4′-dimethylbenzophenone,[5] afforded pinacols on hydrolysis of the anolyte following electrolysis. It was felt, therefore, that "anodic reduction" of diketones having the carbonyl groups separated by varying numbers of methylene groups would give cyclic 1:2-diols (i.e. cyclic pinacols). Furthermore, on the basis of a previously proposed mechanism for the anodic oxidation of magnesium,[1] it was anticipated that there would be a correlation between the initial mean valence number with which the metal entered solution and the size of the carbocylic ring of the diol formed. As a matter of fact, both expectations were realized.

With every diketone, "anodic reduction" and subsequent hydrolysis of the anolyte yielded a 1:2-diol as evidenced by titration with standard lead tetra-acetate solution. The most intensive studies were carried out with 1:3-dibenzoylpropane ($n = 3$) as the organic additive. Hydrolysis of the anolyte yielded a cyclic diol to which Criegee *et al.*[9] have assigned the structure *cis*-1:2-diphenyl*cyclo*pentane-1:2-diol (I) on the basis of its very rapid rate of cleavage with lead tetraacetate solution and its color reaction with potassium "triacetylosmate." However, owing to the fact that only one of the geometrical isomers has ever been prepared, it seemed desirable to provide more substantial evidence for the configuration. That the compound actually possessed the *cis* structure was proved by the demonstration of the existence of intramolecular hydrogen bonding according to the infrared spectral method of Kuhn,[10,11] by the formation of the *iso*propylidene derivative of the *cyclo*pentanediol,[12,13] and the conversion of the diol to the appropriate cyclic ester with phenylboronic acid.[14] Although acid-catalyzed hydrolysis of the *iso*propylidene derivative gave only 2:2-diphenyl*cyclo*pentanone as a result of a pinacol-pinacolone rearrangement, alkaline hydrolysis of the phenylboronate ester afforded the original *cis* diol.

With 1:4-dibenzoylbutane ($n = 4$) as organic additive the situation was more complex than with 1:3-dibenzoylpropane. In addition to the formation of a cyclic

---

[8] D. L. Burdick, A. V. Santoro, W. E. McEwen and J. Kleinberg, *J. Amer. Chem. Soc.* **79**, 5467 (1957).

[9] R. Criegee E. Hoger, G. Huber, P. Kruck, F. Marktscheffel and H. Schellenberger, *Liebigs Ann.* **599**, 81 (1956).

[10] L. P. Kuhn, *J. Amer. Chem. Soc.* **74**, 2492 (1952).

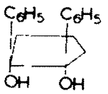
[11] L. P. Kuhn, *J. Amer. Chem. Soc.* **76**, 4323 (1954).

[12] H. G. Derx, *Rec. Trav. Chim.* **41**, 318 (1922).

[13] J. Böeseken, *Bull. Soc. Chim. Fr.* (4) **53**, 1332 (1933).

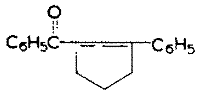
[14] J. M. Sugihara and C. M. Bowman, *J Amer. Chem. Soc.* **80**, 2443 (1958).

1:2-diol, there was obtained 1-benzoyl-2-phenyl-1-*cyclo*pentene(II), a product formed by intramolecular condensation and dehydration of the starting ketone. The reduction product, 1:2-diphenyl*cyclo*hexane-1:2-diol, had the *cis* configuration as



I

shown by formation of the appropriate cyclic ester with phenylboronic acid and the appearance of absorption bands in the infrared spectrum denoting intramolecular hydrogen bonding.



II

Although the 1:2-diols were not actually isolated when the other diketones of the series were used as additives, there was obtained infrared evidence that the "anodic reduction" product of 1:8-dibenzoyloctane ($n = 8$) was a 1:2-diphenyl*cyclo*decane-1:2-diol. It seems reasonable to assume, on the basis of the evidence cited above for the *cyclo*pentane and *cyclo*hexane diols, that all of the diketones investigated gave cyclic *cis* diols.

It is significant that there was found a striking correlation between the initial mean valence number (V_i) of the magnesium entering solution from the anode and the stability of the ring of the 1:2-diol formed by "anodic reduction." The lowest V_i values were obtained in those instances where the diketones originally in solution gave the most stable cyclic diols, i.e. those containing five- and six-membered rings. Moreover, as the data of Fig. 1 show, there is a remarkable similarity between the curve obtained when V_i is plotted against ring size ($n + 2$) and those found when rate or equilibrium data of other reactions involving either the use or formation of ring compounds are plotted as functions of ring size.[11,15–18]

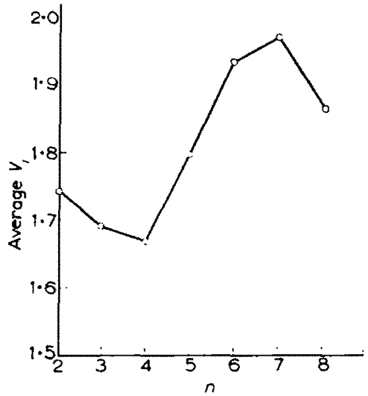


FIG. 1. Anodic behavior of magnesium metal in the presence of various diketones having the general formula $C_6H_5CO(CH_2)nCOC_6H_5$

---

[15] V. Prelog, *J. Chem. Soc.* 420 (1950).

[16] H. C. Brown, R. S. Fletcher and R. B. Johannesen, *J. Amer. Chem. Soc.* 73, 212 (1951).

[17] H. C. Brown and M. Borkawski, *J. Amer. Chem. Soc.* 74, 1894 (1952).

[18] R. Heck and V. Prelog, *Helv. Chim. Acta* 38, 1541 (1955).

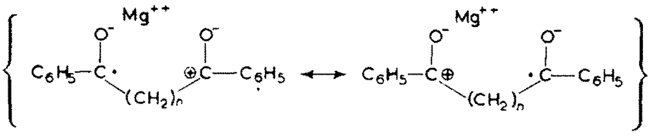
It is also of significance that the anolyte solutions following electrolyses in which the organic oxidant was 1:3-dibenzoylpropane were capable of corroding the massive magnesium employed as anode, whereas solutions of the diketone itself could not do so. The product of corrosion was *cis*-1:2-diphenyl*cyclo*pentane-1:2-diol(I), the same as obtained from electrolysis alone. Evidence of the same general nature as that provided previously in a study of the "anodic reduction" of benzophenone[8] was obtained which showed that the corrosion process proceeded by a free radical chain reaction. (See Experimental for details.)

The following mechanism is proposed to account for both the electrolytic and corrosion results cited above:

(1) The magnesium anode enters solution at least in part in the +1 state.[1]

(2) Part of the unipositive magnesium is oxidized to the common +2 state by diketone and part electrochemically at the surface of the anode. The relative rates of these competing reactions determine the initial mean valence number (V_i) observed in each experiment.

(3) To explain the variation of V_i with ring size of the product of "anodic reduction," it seems reasonable to assume that the diketone and the +1 magnesium react to give intermediate III.

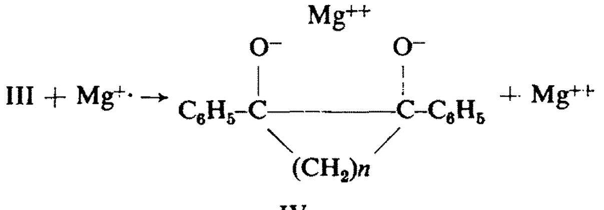


III

The stability and ease of formation of (III) is greatest when $n = 3$ or 4, and therefore, as a result of the competitive oxidation of unipositive magnesium given in (2), the V_i values are the lowest when the diketones are 1:3-dibenzoylpropane and 1:4-dibenzoylbutane.

(4) Before the magnesium salt (IV) of the ultimate cyclic diol can be formed, intermediate (III) must gain an additional electron. In the "anodic reduction" process, this extra electron can be provided by unipositive magnesium, whereas in the corrosion process the electron is obtained from massive magnesium:

"anodic reduction" process



IV

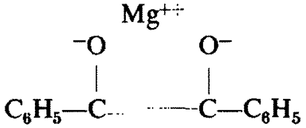
corrosion process (chain mechanism)

(a) $\text{III} + \underset{\text{(massive)}}{\text{Mg}} \rightarrow \text{IV} + \text{Mg}^{+\cdot}$

(b) $C_6H_5CO(CH_2)_nCOC_6H_5 + \text{Mg}^{+\cdot} \rightarrow \text{III} + \text{Mg}^{++}$

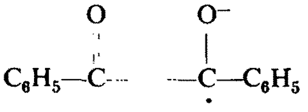
It is likely that any of the intermediate (III) which is still present at the time of hydrolysis undergoes disproportionation to give the cyclic diol plus the original diketone.

As reported previously,[5] benzil on "anodic reduction" gives benzoin in quantitative yield. It is probable that the magnesium enolate(V) is the final reduction product existing in the anolyte prior to hydrolysis; it is clear that (V) may be regarded as the same general type of compound as (IV), but one in which $n = 0$. Furthermore, evidence has now been obtained that the radical-ion(VI) is formed by the initial reaction of unipositive magnesium with benzil. The species (VI) functions as a chain carrier in corrosion of massive magnesium following electrolysis.* The organic corrosion product, following hydrolysis of the reaction mixture, is also benzoin. Thus in "anodic reduction" and in subsequent corrosion behavior benzil acts in a manner strictly analogous to that of 1:3-dibenzoylpropane and presumably the other diketones investigated.



$$\overset{Mg^{++}}{C_6H_5-\overset{^{-}O}{\overset{|}{C}}\cdots\cdots\overset{O^{-}}{\overset{|}{C}}-C_6H_5}$$

V



$$C_6H_5-\overset{O}{\overset{\vdots}{C}}\cdots\cdots\overset{O^{-}}{\overset{|}{\underset{\bullet}{C}}}-C_6H_5$$

VI

Whereas the mechanism of "anodic reduction" presented above and in our previous papers is completely consistent with all the data thus far accumulated, it has been pointed out to us by the referee of a previous paper that there is a possible alternative mechanism, namely one involving simultaneous anodic-cathodic behavior of the magnesium rod which is normally regarded as the anode. On the basis of evidence published to date there is no way of distinguishing between these alternatives. However, although this matter is still open, it seems to us that the corrosion mechanism which involves unipositive magnesium as a chain carrier is firmly established.[8]

EXPERIMENTAL†

Materials. The 0·5 cm (diameter) magnesium rods which were used as the electrodes were cut from an 0·8 cm rod of 99·8% purity furnished by the Aluminum Company of America. The sodium iodide, "Baker's Analyzed," which was employed as the electrolyte was dried at a temp of 110° for several days before use. Pyridine, Mallinckrodt Analytical Reagent grade was fractionally distilled at atmospheric pressure from sodium through a 45 cm packed column and stored over anhydrous barium oxide. By an adaptation of a procedure described in *Organic Syntheses*[19] each of the following diketones was prepared: 1:3-dibenzoylethane, 1:4-dibenzoylpropane, 1:5-dibenzoylpentane, 1:6-dibenzoylhexane, 1:7-dibenzoylheptane, and 1:8 dibenzoyloctane. The melting points of the diketones agreed with the values

---

* For previous evidence regarding the existence of radical-ion (VI) see B. Venkataraman and G. K. Fraenkel, *J. Amer. Chem. Soc.* 77, 2707 (1955) and J. L. Ihrig and R. G. Caldwell, *J. Amer. Chem. Soc.* 78, 2097 (1955).

† All melting points are corrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[19] R. C. Fuson and J. T. Walker, *Organic Syntheses* (2nd Ed.) Coll. Vol. II, p.169. Wiley, New York (1943).

reported in the literature.[19–21] 1:2-Dibenzoylbutane was prepared by the reduction of 1:4-diphenyl-1:4-butenedione with stannous chloride.[21]

Apparatus and procedure. The divided cell used in the electrolyses was of the same type described by Davidson and Jirik.[22] The source of direct current was a full-wave mercury tube rectifier capable of supplying up to 1000 volts. A silver coulometer in series with the cell was employed to determine the quantity of current passed. The cell and its contents were immersed in a water bath which was maintained at 40 ± 0·1°.

Before an electrolysis the magnesium electrodes (0·5 cm × 5 cm) were throughly cleaned with dilute nitric acid, washed with distilled water, and then dried and weighed. The sodium iodide solution (0·5 m in pyridine) was prepared in such a manner as to minimize exposure to air and moisture. For most experiments, 0·025 mole of diketone was dissolved in 100 ml of the sodium iodide-pyridine solution and then half of the resulting solution was added to each compartment of the electrolytic cell. The cell was swept with dry oxygen-free nitrogen both before and during each electrolysis. The duration of electrolysis, the applied voltage, and the current density will be specified below for the various types of experiments. On completion of electrolysis, the anode was washed successively with distilled water, acetone and distilled water. After the electrode had been dried and weighed, the initial mean valence number (V_i) was calculated in accordance with the equation

$$V_i = \frac{\text{wt of Ag deposited in coulometer} \times 24{\cdot}32}{107{\cdot}88 \times \text{wt of Mg lost from anode}}$$

Effect of nature of diketone on initial mean valence number. Four to six electrolyses were carried out with each diketone. Each electrolysis was conducted for a period of 2 hr at an applied voltage of 25–45 volts and an anodic current density of 0·003–0·006 amp/cm^2. The average initial mean valence numbers obtained with the various diketones were as follows: 1:2-dibenzoylethane, 1·74 ± 0·02; 1:3-dibenzoylpropane, 1·69 ± 0·01; 1:4-dibenzoylbutane, 1·67 ± 0·02; 1:5-dibenzoylpentane, 1·80 ± 0·04; 1:6-dibenzoylhexane, 1·93 ± 0·05; 1:7-dibenzoylheptane, 1·97 ± 0·03; 1:8-dibenzoyloctane, 1·87 ± 0·01.

"*Anodic reduction*" *of* 1:3-*dibenzoylpropane.* Electrolyses in which 1:3-dibenzoylpropane (0·025 m) was the organic additive gave initial mean valence numbers (V_i) for magnesium of 1·63 and 1·53. The time of electrolysis in each case was 24 hr, the applied voltage 25–50 volts, and the initial current density 0·005–0·007 amp/cm^2. On completion of each electrolysis, the contents of anolyte and catholyte were drained into separate flasks each containing 125 ml of freshly boiled 18% HCl cooled to 0° with cracked ice. The resulting anolyte solution was placed in a refrigerator for 24 hr and the precipitate which had formed collected by filtration. The filtrate was extracted with ether in a continuous extractor, and the precipitate was combined with the material recovered from the ether extract. The combined solid material was dissolved in chloroform and diluted to a volume of 250 ml.

---

[20] L. A. Wiles and E. C. Baughan, *J. Chem. Soc.* 933 (1953).
[21] P. S. Bailey and R. E. Lutz, *J. Amer. Chem. Soc.* **70**, 2412 (1948).
[22] A. W. Davidson and F. Jirik, *J. Amer. Chem. Soc.* **72**, 1700 (1950).

Appropriate aliquots were withdrawn, evaporated to dryness, and the quantity of 1:2-diol determined by titration with lead tetraacetate according to the procedure of Gebhart and Adams.[23] The lead tetraacetate solution was standardized against *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol, prepared as described below. The yields of 1:2-diol, as found by titration, were 94% for the electrolysis which gave a V_i of 1·63 and 92% for that in which the V_i equalled 1·53, the theoretical yield being determined by the use of the equation:

$$\text{wt of 1:2-diol} = \frac{(2 - V_i)\,(\text{wt of Mg lost from anode})}{24{\cdot}32} \times \text{equiv. wt of 1:2-diol}$$

The yields were calculated on the assumption that the 1:2-diol formed was *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol. As is shown below this assumption was a valid one.

Isolation of cis-1:2-*diphenyl*-1:2-cyclo*pentanediol from anolyte hydrolysate.* In an experiment designed to facilitate the isolation of the 1:2-diol, 2·0 g of 1:3-dibenzoylpropane was added to the sodium iodide-pyridine solution contained in the anode compartment. No organic additive was dissolved in the catholyte. Electrolysis was carried out for 16 hr under the same conditions as in the previous experiment; a V_i value of 1·35 was found.

The anolyte solution was hydrolyzed as described above, the resulting solution placed in a refrigerator for 24 hr, and then the precipitate (A) present filtered off. The filtrate was subjected to continuous extraction with ether and the resulting ether solution then washed with small amounts of dilute aqueous solutions of sodium besulfite, hydrochloric acid, sodium bicarbonate, and finally distilled water. Removal of the ether by distillation left 0·40 g of a solid material, which was dissolved in chloroform. The infrared spectrum of this solution was taken and found to be essentially identical with that of a chloroform solution of authentic *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol (see below). Moreover, addition of petroleum ether (b.p. 38°) to the chloroform solution yielded 0·25 g of a crystalline material, m.p. 102–103°, which did not depress the melting point of authentic *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol.

The original precipitate (A) was dissolved in chloroform and an appropriate aliquot titrated with standard lead tetraacetate solution as described previously. The precipitate was found to contain 0·14 g of 1:2-diol. The infrared spectrum of the chloroform solution showed that precipitate (A) consisted of a mixture of starting diketone (1:3-dibenzoylpropane) and *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol.

The total yield of *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol amounted to 0·54 g (theoretical 0·62 g, as calculated by the equation given in previous section).

cis-1:2-*Diphenyl*-1:2-cyclo*pentanediol.* By a method adapted from one described by Japp and Michie,[24] 1:3-dibenzoylpropane was reduced to a 1:2-diol which was identical with that obtained by "anodic reduction" of the diketone. After 2·00 g (0·074 mole) of aluminum foil had been cut up into pieces 1 cm in length, it was treated with a dilute aqueous solution of mercuric chloride for 2 min. The amalgamated aluminum pieces were collected by filtration, washed with ethanol and ether, and added to 200 ml of aqueous ethanol containing 67% (by volume) of the

---

[23] H. J. Gebhart, Jr. and K. H. Adams, *J. Amer. Chem. Soc.* **76**, 3925 (1954).

[24] F. R. Japp and A. C. Michie, *J. Chem. Soc.* **79**, 1020 (1901).

alcohol. To this mixture was added 5·00 g (0·002 mole) of 1:3-dibenzoylpropane, and the mixture was heated with stirring for 3 hr at a temp. slightly below the boiling point of ethanol. An additional 0·5 g of the amalgamated aluminum was added to the mixture, which was then stirred overnight. The mixture was heated to boiling and filtered hot. After the filtrate had been concentrated to one-third of its original volume, 2·5 g of the 1:2-diol crystallized from solution. The purified material had a m.p. of 102–103°; reported, 101°.[9]

(Found: C, 80·06; H, 7·19; Calc. for $C_{17}H_{18}O_2$: C, 80·32; H, 7·08%).

The elemental analysis, the fact that the infrared spectrum of the compound taken in chloroform solution showed the presence of hydroxyl groups but the absence of carbonyl groups, the oxidation of the compound to the original diketone by means of chromic acid,[24] and the quantitative cleavage by lead tetraacetate prove conclusively that the compound is ether *cis*- or *trans*-1:2-diphenyl-1:2-*cyclo*pentanediol.

While experiments to determine the configuration of the diol were in progress in this Laboratory, Criegee *et al.*[9] claimed that the compound possessed the *cis* configuration on the basis of its rapid rate of reaction with lead tetraacetate and the fact that it gave a positive color reaction with potassium "triacetylosmate." Inasmuch as only one isomer is known, the evidence for the *cis* configuration would appear not to be entirely conclusive. Therefore, several additional lines of evidence pertaining to the configuration were uncovered.

Infrared evidence for intramolecular hydrogen-bonding. The infrared evidence that the cyclic 1:2-diol possessed the *cis* configuration was obtained by the procedure of Kuhn.[10] In 50 ml of reagent grade carbon tetrachloride that had been dried over phosphorus pentoxide was dissolved 0·2523 g (0·001 mole) of the diol, m.p. 102°–103. Aliquots of this solution were taken and diluted to give a series of solutions of concentrations 0·002, 0·004, 0·01, and 0·02 M. Infrared spectra were taken and all four of the solutions showed absorption peaks at 3600 and 3540 cm^{-1}. Furthermore, the relative intensities of the peaks were essentially constant, showing that the hydrogen bonding which gives rise to the absorption peak at 3540 cm^{-1} is intramolecular and that the cyclic diol has the *cis* configuration.

Preparation of cis-1:2-*diphenyl*-1:2-cyclo*pentanediol phenylboronate.* To 1·12 g (0·009 mole) of phenylboronic acid dissolved in 4 ml of methanol was added 0·90 g (0·0035 mole) of the 1:2-diol, m.p. 102–103°. After warming to effect reaction, the mixture was cooled, filtered, and the precipitate washed with 10 ml of hot water, 5 ml of cold methanol, and then dried in an oven at 110°. There was obtained 1·06 g (90%) of the ester, which on recrystallization from absolute methanol-benzene had an m.p. of 158·8–159·2°.

(Found: C, 81·31; H, 6·25; B, 3·41; Calc. for $C_{23}H_{21}BO_2$: C, 81·19; H, 6·22; B, 3·18%).

It has been established[14] that *cis*-1:2-*cyclo*pentanediol gives a phenylboronate ester of molecular formula $C_{11}H_{13}BO_2$, whereas the *trans* diol yields an ester of molecular formula $C_{17}H_{18}B_2O_3$. The isomeric 1:2-*cyclo*hexanediols behave analogously. Therefore, inasmuch as the 1:2-diphenyl-1:2-*cyclo*pentanediol of m.p. 102–103° gives a phenylboronate having but one phenylboronate moiety, it can be concluded that the cyclic diol has the *cis* configuration.

Hydrolysis of the phenylboronate. To a solution of 20 ml of dioxane in 100 ml of water was added 6·0 g of sodium hydroxide and 0·5 g of *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol phenylboronate. The resulting solution was refluxed for 1 hr and extracted with ether. After the ether extract had been washed with water and dried over anhydrous sodium sulfate, the ether was removed by distillation and the residue recrystallized from chloroform–petroleum ether solution. There was obtained a white crystalline compound, m.p. 102–103°, which did not depress the melting point of authentic *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol.

Preparation of the iso*propylidine ketal of* cis-1:2-*diphenyl*-1:2-cyclo*pentane-diol.* To a solution of 5·00 g (0·02 mole) of the 1:2-diol, m.p. 102–103°, in 100 ml of highly purified acetone contained in an Erlenmeyer flask, was added 1 ml of conc sulfuric acid. The flask was stoppered tightly and allowed to stand for 12 hr at room temp. Most of the solvent was then removed by distillation under reduced pressure and an aqueous solution containing 5 g of potassium carbonate added. The organic material was extracted into ether, the ether solution dried over anhydrous sodium sulfate and the solvent removed by distillation. The residue was dissolved in petroleum ether, b.p. 38°, and chromographed on alumina. Elution with petroleum ether provided 0·8 g of white solid which had an m.p. of 84–85° after recrystallization from *n*-hexane.

(Found: C, 81·53; H, 7·29; Calc. for $C_{20}H_{22}O_2$: C, 81·58; H, 7·53%).

Hydrolysis and rearrangement of the iso*propylidine ketal.* A solution of 0·2 g of the *iso*propylidine ketal, m.p. 84–85°, in 3·0 ml of 87% formic acid was heated on a steam bath for 50 min. The solution was made alkaline with sodium hydroxide solution and extracted with chloroform. The chloroform solution was dried over anhydrous magnesium sulfate and evaporated, giving 0·158 g of a solid which was identified as a ketone by the presence of an absorption peak at 1730 cm^{-1} in the infrared spectrum taken in chloroform solution. The compound was identified as 2:2-diphenyl*cyclo*pentanone by the preparation of the 2:4-dinitrophenylhydrazone, m.p. 180–181°; reported[25] 182–182·5°.

(Found: C, 66·46; H, 4·87; N, 13·19; Calc. for $C_{23}H_{20}N_4O_4$: C, 66·33; H, 4·84; N, 13·46%).

Numerous attempts were made to effect acid-catalyzed hydrolysis of the ketal in order to obtain the original 1:2-glycol. However, in every case either unchanged ketal or the rearrangement product, the ketone, was found.

Isolation of an ether from "anodic reduction" of 1:3-*dibenzoylpropane.* Following an electrolysis and work-up procedure of the type described under "anodic reduction" of 1:3-dibenzoylpropane, the chloroform solution remaining after an aliquot had been removed for lead tetraacetate titration was evaporated to dryness. The residue was subjected to fractional crystallization from absolute ethanol, and as one of the most soluble fractions there was obtained 0·070 g of a compound having an m.p. of 255·5–256·0° after two recrystallizations from acetone.

(Found: C, 83·29; H, 6·82; Calc. for $C_{34}H_{34}O_3$: C, 83·22; H, 6·98%).

The empirical formula of the compound strongly suggests that it is an ether derived from *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol. It should be emphasized that this small amount of ether represents an anolyte product in addition to the parent 1:2-diol, which was obtained in 92% yield.

---

[25] N. R. Easton and S. J. Nelson, *J. Amer. Chem. Soc.* **75**, 640 (1953).

"Anodic reduction" of 1:4-*dibenzoylbutane.* Electrolyses in which 1:4-dibenzoylbutane was the organic additive were carried under the same conditions as described under "anodic reduction" of 1:3-dibenzoylpropane. The work-up of the anolyte after electrolysis was also identical, up to and including the point where the neutral fraction was isolated as solid.

The neutral solid was dissolved in freshly distilled acetone and made up to a volume of 100 ml. From this stock solution three 5-ml aliquots were withdrawn. Two of the aliquots were used for titration with standard lead tetraacetate solution The third was evaporated to dryness, the residue dissolved in chloroform and the infrared spectrum taken.

In a series of three electrolyses in which the V_i values ranged from 1·52–1·60, the yields of 1:2-diol varied from 39·2 to 49·8 per cent. In each case the infrared spectrum indicated that products other than the diol had also been formed.

Following two electrolyses in which the V_i values were 1·52 and 1·60, the acetone solutions remaining after the aliquots noted above had been removed were combined and evaporated to dryness. The residue, which amounted to 4·34 g, was dissolved in 25 ml of hot petroleum ether (b.p. 38°) and the solution cooled and filtered. The precipitate which had formed was recrystallized from 25 ml of absolute methanol and there was obtained 1·97 g of starting diketone, m.p. 105–106°. The petroleum ether and methanol mother liquors were combined, evaporated to dryness, dissolved in anhydrous benzene, and chromatographed on 100 g of alumina. The column was developed with anhydrous benzene and adsorbed material eluted first with benzene and then with a 5% solution of methanol in benzene. Finally, the alumina was thoroughly extracted with methanol in a Soxhlet extractor.

Two products were obtained from the benzene eluant. The first compound to come through the column amounted to 1·18 g and had an m.p. of 42·4–43·4° after recrystallization from petroleum ether. This compound was identified as 1-benzoyl-2-phenyl-1-*cyclo*pentene(II) by means of a mixed melting point test with authentic II (see below), as well as by the identity of the infrared spectra taken in chloroform solution. The second product (0·43 g) was found to be starting diketone.

The third compound isolated, by elution with methanol-benzene, weighed 0·66 g. Following recrystallization from low boiling petroleum ether, the compound had an m.p. of 73·2–73·9°.

(Found: C, 80·31; H, 7·54; Calc. for $C_{18}H_{20}O_2$: C, 80·56; H, 7·51%).

This compound was identified as *cis*-1:2-diphenyl*cyclo*hexane-1:2-diol by the demonstration of the existence of intramolecular hydrogen bonding by the same method as employed with *cis*-1:2-diphen*cyclo*pentane-1:2-diol and by the preparation of the appropriate phenylboronate ester (see below).

Extraction of the alumina with methanol gave 0·08 g of a compound which was not identified but the infrared spectrum of which contained a peak at 1680 cm^{-1}, indicating the presence in the compound of a carbonyl group.

It is probable that a competing "anodic reduction" process, namely reduction of the water formed by intramolecular condensation of 1:4-dibenzoylbutane to give 1-benzoyl-2-phenyl-1-*cyclo*pentene, accounts for the relatively low yield of the diol.

Synthesis of 1-*benzoyl*-2-*phenyl*-1-cyclo*pentene.* To a solution of 13·3 g (0·05 mole) of 1:4-dibenzoylbutane in 200 ml of anhydrous benzene was added 3·9 g (0·1 mole) of sodium amide. The mixture was stirred for a few min at room temp and then heated on a steam bath for 3 hr. About 150 g of ice was added, and the mixture permitted to stand overnight. The benzene layer was removed, washed with water, dried over anhydrous sodium sulfate, and the solvent removed by distillation. The residual oil was distilled at 1 mm press and the fraction of b.p. 155–164° was collected. When the oil was dissolved in hot low boiling petroleum ether and the solution allowed to cool, crystalline 1-benzoyl-2-phenyl-1-*cyclo*pentene was obtained and found to have an m.p. of 43·4–44·4°.

(Found: C, 86·91; H, 6·59; Calc. for $C_{18}H_{16}O$: C, 87·06; H, 6·49%).

The infrared spectrum of the compound in chloroform solution showed an absorption peak at 1645 cm^{-1} and was consistent in other respects with an α-β-unsaturated ketone structure.

cis-1:2-*Diphenyl*-1:2-cyclo*hexandiol phenylboronate*. To a solution of 50 mg of phenylboronic acid in 0·5 ml of absolute methanol was added 20 mg of the 1:2-diol, m.p., 73·2–73·9°. After the solution had been permitted to stand for several days at 0°, a white crystalline material precipitated. Its m.p. was 127–128° after recrystallization from absolute methanol.

(Found: C, 81·45; H, 6·61; B, 3·18: Calc. for $C_{24}H_{23}BO_2$: C, 81·37; H, 6·54; B, 3·05%).

Summary of yields of 1:2-*diols*. Although no attempts were made to isolate "anodic reduction" products of the diketones listed below, the following yields of 1:2-diols were determined by duplicate lead tetraacetate titrations:

Diketone	Yield of 1:2-diol%
1:2-dibenzoylethane	40
1:5-dibenzoylpentane	50
1:6-dibenzoylhexane	88
1:7-dibenzoylheptane	71
1:8-dibenzoyloctane	77

It should be emphasized that, owing to the relatively high V_i values (Fig. 1), the quantities of diols formed were very small and, therefore, the yields reported above are subject to relatively large errors.

"*Anodic reduction*" *of* 1:8-*dibenzoyloctane*. Following an electrolysis in which 1:8-dibenzoyloctane was present as additive and in which the theoretical yield of 1:2-diphenyl-1:2-*cyclo*decanediol was calculated to be 88 mg, the anolyte hydrolysate was worked up in the same manner as described for the 1:4-dibenzoylbutane electrolysis. The material eluted with methanol-benzene could not be crystallized, but the infrared spectrum of the material (in chlorofoim) indicated that the 1:2-diol had been concentrated in this fraction. The fact that there was absorption in the spectrum at both 3550 and 3590 cm^{-1} was consistent with the occurrence of hydrogen bonding.

Products formed at the cathode. It has already been shown that the cathodic reduction of benzil at a magnesium cathode in pyridine gives a quantitative yield of benzoin.[5] With diketones of the type in which two or more methylene groups separated the benzoyl groups attempts to isolate products from the catholyte hydrolysate gave highly colored, intractable material in every case. Titration of these materials with lead tetraacetate showed the presence of very small amounts of 1:2-diols (1–15%).

Corrosion experiments. Solutions of the diketones in sodium iodide-pyridine did not attack massive magnesium prior to electrolysis. However, in the two cases which were studied, namely with 1:3-dibenzoylpropane and benzil as additives, the anolyte solutions following electrolysis were capable of corroding the massive metal.

After an electrolysis in which 1:3-dibenzoylpropane was the additive and in which the V_i was 1·69, with 0·2752 g of magnesium entering solution from the anode, a freshly cleaned, weighed magnesium rod was placed in the anolyte. The rod was permitted to stand in the solution for a period of 123 hr, after which it was cleaned, dried and weighed. The loss in weight of the rod corresponded to the dissolution of 0·0071 g atom of magnesium. Inasmuch as the calculated quantity of radical-ion(III) ($n = 3$) produced during the electrochemical process was but 0·0035 g mole, it is evident[8] that corrosion occurred by a chain mechanism. The anolyte was hydrolyzed and worked up as described under "anodic reduction" of 1:3-dibenzoylpropane. The lead tetraacetate titration accounted for 70% of the *cis*-1:2-diphenyl-1:2-*cyclo*pentanediol expected from a combination of electrolysis and corrosion by the chain mechanism described in the theoretical section. In a second corrosion experiment the pertinent data were: V_i, 1·71; loss of weight of anode during electrolysis, 0·1845 g; time of corrosion, 87 hr; loss in weight of magnesium rod during corrosion, 0·0073 g atom; calculated quantity of radical-ion produced during electrolysis, 0·0022 g mole; yield of diol as determined by lead tetraacetate titration, 73%. On the basis of calculations with the data from the second corrosion experiment, 6·6 times more magnesium was brought into solution in the corrosion process than would have been theoretically possible if the latter had occurred by the other than a chain mechanism.

Pertinent data for three corrosion experiments subsequent to electrolyses in which benzil was the additive follow: V_i, 1·48, 1·37, 1·62; loss of weight of anode during electrolysis, 0·4534, 0·5240, 0·1506 g; time of corrosion, 93, 336, 68 hr; loss in weight of magnesium rod during corrosion, 0·0131, 0·0106, 0·0115 g atom; calculated quantity of radical-ion (VI) produced during electrolysis, 0·0097, 0·0133, 0·0030 g mole. These data are definitely in accord with a chain mechanism for corrosion. Analysis of one of the reaction mixtures by the infrared method described previously[5] accounted for 81% of the benzoin expected from a combination of electrolysis and corrosion by the chain mechanism described in the theoretical section. Unlike the experiment with 1:3-dibenzoylbutane, there was a significant degree of corrosion of massive magnesium in the catholyte following electrolysis.

Acknowledgment—The authors are indebted to the Office of Ordnance Research, U.S. Army, for a research grant which has made this investigation possible.