Experimental Section

Sources or syntheses of the various materials employed have been previously described[1] excepting the following: Eastman white label 2-pentanol was used as received. Pyridine and trifluoroacetic acid were research grade materials and were used as received. Benzaldehyde-7-C^{14} was purchased from Nuclear-Chicago Corporation, Chicago, Illinois, diluted with unlabeled research grade material, base-washed, dried, and distilled to yield a material of 4867 dpm/mg activity. *meso*-Hydrobenzoin (mp 137°) was prepared by the sodium borohydride reduction of benzil.[15] *dl*-Hydrobenzoin (mp 120°) was prepared from reagent grade *trans*-stilbene utilizing the sequence: epoxide[16] → hydrobenzoin monotrichloroacetate[6] → hydrobenzoin.[6] The labeled hydrobenzoin employed was the highest level material obtained from the various dilution studies. Radioactivities were measured on a Tri-Carb Scintillation Counter (Packard Instrument Co., Inc.). Melting points were determined on a Kofler hot stage and are uncorrected.

A prototype Griffin-Srinivasan photoreactor employing a vertically mounted circle of 12 Sylvania F8T5 (BLB) lamps was used in all cases. The spectrum emitted by a representative lamp has been reported.[1] Air jets from the bottom of the reactor maintained an ambient temperature of approximately 40°. Pyrex glassware was used exclusively.

General Procedure.—The general procedure was essentially as previously described,[1] excepting that no acetic acid was present in the alkaline media, and heptane was found to be a more satisfactory solvent than hexane for the recrystallization of the products. Solutions were essentially 10% in ketone; solvent plus any additives other than ketone totalled 10 ml. Subsequent to irradiation, all alkaline runs were neutralized with glacial acetic acid prior to dilution with methanol to the prescribed 100 ml. The *dl*-acetophenone pinacol was recrystallized to a final melting point of 125° and the *meso* diastereomer to a melting point of 121°. The *dl*-hydrobenzoin was recrystallized to a melting point of 120°, and the *meso* form to a melting point of 137°. The results, including the various modifications in general procedure, are tabulated in Table I.

Registry No.—Acetophenone-7-C^{14}, 5821-66-9; benzaldehyde-7-C^{14}, 14734-27-1.

Acknowledgment.—The authors wish to express appreciation for financial support from the U. S. Atomic Energy Commission under Contract AT-(40-1)-2833, (ORO-2833-13).

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[15] L. F. Fieser, "Organic Experiments," D. C. Heath and Co., Boston, Mass., 1964, pp 216.

[16] A. C. Cope, P. A. Trumbull, and E. R. Trumbull, *J. Am. Chem. Soc.*, **80**, 2844 (1958).

Quantitative Studies in Stereochemistry C. Electrochemistry. I. The Ratio of Diastereomeric Pinacols Formed in the Electrolytic Bimolecular Reduction of Acetophenone-7-C^{14}

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The electrolytic bimolecular reduction of acetophenone in acidic aqueous ethanol produced approximately equal amounts of the diastereomeric 2,3-diphenyl-2,3-butanediols. The corresponding reduction in basic media afforded the same pinacols in a 3:1 *dl/meso* ratio. Mercury, tin, and copper cathodes all gave essentially the same ratios of diastereomers. The stereochemistry also appeared to be independent of time, use of controlled potential, use of constant current, and current level. The pinacols themselves proved stable to the alkaline media employed.

The preparation of specific diastereomers of *sym*-tetrasubstituted glycols (pinacols) may be attempted by several synthetic routes; probably favored among them is the double addition of organometallic reagents to α-diketones.[1,2] The utility of this method is limited by the availability of the diketones, the degree of stereoselectivity involved, and the nonreliability of methods for predicting the predominant diastereomer.

What should be the most attractive route, the bimolecular reduction of unsymmetrical ketones, utilizing readily available compounds, has been carried out employing metals in appropriate solvents,[3] ultraviolet light,[4] and electrolytic techniques.[5] There are essentially no data available adequately describing the stereoselectivity, if any, of these possible choices where pinacol formation is involved.[6,7] A careful examination of those reports in which electrolytic techniques were employed to yield a pinacolic product of narrow melting point range in greater than 50% yield, and where diastereomeric forms were possible, suggested strongly that in some cases the reaction was stereoselective. This statement does not, however, appear to have been made explicitly. Concomitantly, satisfactory stereochemical identification of the pinacols

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[1] (a) J. H. Stocker, P. Sidisunthorn, B. M. Benjamin, and C. J. Collins, *J. Am. Chem. Soc.*, **82**, 3913 (1960), and references cited therein; (b) J. H. Stocker, *J. Org. Chem.*, **29**, 3593 (1964); (c) J. H. Stocker, *J. Am. Chem. Soc.*, **88**, 2878 (1966).

[2] The obvious possibility of the stereospecific hydroxylation of tetrasubstituted ethenes has been excluded on the basis of the available data. A careful examination of the extensive tables included in the chapter on Hydroxylation Methods by F. D. Gunstone ["Advances in Organic Chemistry," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1960] discloses but two examples of such hydroxylations, both involving cycloalkenes. Several attempts by the senior author have uniformly met with failure.

[3] H. Gilman, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, pp 459 ff; M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, **49**, 236 (1927). Many other examples might be cited.

[4] P. deMayo, "Advances in Organic Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, pp 367–427; J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, pp 523 ff; A. Schonberg, "Präparative Organische Photochemie," Springer Verlag, Berlin, 1958, pp 109 ff.

[5] S. Swann, Jr., "Technique of Organic Chemistry," Vol. II, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1956, pp 495–496, and references cited therein.

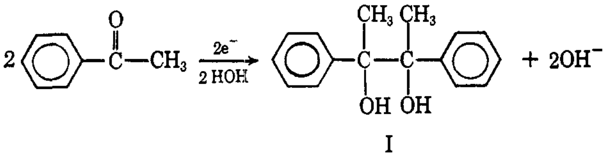
[6] J. H. Stocker and D. H. Kern [*J. Org. Chem.*, **31**, 3755 (1966)] have quantitatively described the stereochemistry of the *photochemical* bimolecular reduction of acetophenone.

[7] J. Grimshaw and J. S. Ramsey [*J. Chem. Soc., Sect. C*, 653 (1966)] have described semiquantitatively (based on chemical isolation) the stereochemistry of the electrolytic bimolecular reduction of several hydroxybenzaldehydes. This article provides useful references to earlier work. M. Lund [*Acta Chem. Scand.*, **11**, 283 (1957)] has examined the electrolytic bimolecular reduction of several keto steroids and found stereoisomers were produced, the relative amounts of each a function of the pH of the media.

involved, as well as fully quantitative data, is lacking.[7,8]

The present paper, to be the first of several, offers quantitative data for the acetophenone system, as determined by isotope dilution techniques. The choice of acetophenone as the pinacol precursor was attractive for several reasons; it is commercially available in labeled form, synthetic routes to the pure diastereomeric pinacols have been reported,[1a] and the stereochemical identity of the individual diastereomers has been unequivocally demonstrated.[9]

The stoichiometry of the over-all reaction in aqueous solution is given by eq 1 where I represents both the



(1)

I

meso and *dl* forms possible. The stereochemistry of only the dimerization step is under consideration; the sequence of preceding steps will be considered in future papers.

The most extensive studies of the macroscale electrolytic reduction of acetophenone have been those of Swann and his co-workers.[10,11] Without examining the stereochemistry of the reaction, they determined that the major products in acidic aqueous methanol were the pinacol, the bis-α-methylbenzyl ether, and appreciable amounts of high-boiling or nondistillable materials. In alkaline media, the pinacol was the major product (customarily 30–50%), with unspecified but "never very high" yields of the monomolecular reduction product, the carbinol. The over-all yield appeared to depend on the cathode utilized. Pasternak[12] and Elving and Leone[13] have also carried out macroscale electrolytic reductions of acetophenone both in acid and base; these workers isolated or claimed both pinacols and carbinol, the latter "predominating" at intermediate pH values (7–10).

Any examination of the pertinent stereochemistry might consider the following experimental variables: pH, current level, reaction time, reactant concentration, temperature, use of constant current or controlled potential, and choice of electrode, electrolyte, and solvent. The present paper provides some experimental information on all of these excepting temperature and solvent effects.

Preliminary work to establish suitable reduction potentials was carried out polarographically and verified that the several values reprinted by Kolthoff and Lingane[14] for the half-wave potential of acetophenone as a function of pH could be used satisfactorily. These varied from an $E_{1/2}$ of 1.12 at pH 1.3 to 1.33 at 4.9, 1.58 at 7.2, 1.62 at 8.6, and 1.64 at 11.3. It may be noted that there is very little change of $E_{1/2}$ with pH above 7.

The initial studies were carried out under controlled potential conditions with an Analytical Instrument Co. potentiostat coupled with a current integrator. Since the emphasis in the present study was best served by maximizing the yields, no attempt was made to compare yields with coulombs used and reaction times chosen were either a matter of convenience or to correlate with previous studies.

Ethanol (80%) was selected as the solvent for solubility reasons.[15] This limited the choice of buffers and made the most difficult aspect of the work pH control. While the use of this alcoholic medium made absolute evaluation of pH uncertain, its use throughout the study suggested that the relative ratios obtained should be adequately meaningful.[16] As indicated by the equation above, the medium became increasingly alkaline with time. For the acid runs (see Table I), this did not prove to be a source of concern; under representative conditions, an initial pH of 4.2 would rise to about 5.5 in a 10-hr period. For the alkaline runs, however, an initial value of approximately 8 would reach a pH of 12 (both values determined on a pH meter) within 30 min. Efforts to find satisfactory buffer systems in the critical region of pH 9–12 were not successful. Accordingly, no attempt has been made to describe the exact acidities of most individual runs; these may be adequately divided into "below 7" and "above 12" with the specific exceptions noted.

The experimental results are tabulated in Table I.

Results and Discussion

A perusal of Table I will suggest the following general conclusions.

(a) The reduction shows some stereoselectivity.

(b) The stereochemistry of the reduction is pH dependent.

(c) The diastereomeric ratios may be divided conveniently into two general categories, 0.9–1.4 *dl/meso* and 2.5–3.2 *dl/meso*, corresponding to "acidic" and "basic" media, respectively.[17]

(d) The diastereomeric ratios are clearly independent of the choice of cathodes (mercury, tin, or copper).

(e) The several parameters (time, use of constant potential, constant current, or level of current) do

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[8] In a number of cases, pairs of otherwise unidentified diastereomeric pinacols have been nonquantitatively isolated by chemical means: *e.g.*, M. J. Allen, J. E. Fearn, and H. Levine, *J. Chem. Soc.*, 2220 (1952); M. J. Allen, *ibid.*, 1598 (1951); G. I. Hobday, *ibid.*, 609 (1943); C. C. Price, *J. Am. Chem. Soc.*, **66**, 634 (1944). Various pairs of diastereomeric α-glycols, predominantly hydrobenzoins, have similarly been isolated from the corresponding aldehydes; *cf.*, *e.g.*, M. J. Allen, *J. Org. Chem.*, **15**, 435 (1950).

(9) D. J. Cram and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 2748 (1959).

(10) S. Swann, Jr., and G. H. Nelson, *Trans. Electrochem. Soc.*, **67**, 201 (1935) (studies in acidic solution).

(11) S. Swann, Jr., P. E. Ambrose, R. C. Dole, R. C. Rowe, H. M. Ward, H. D. Kerfman, and S. Axelbrod, *ibid.*, **85**, 231 (1944) (studies in alkaline solution).

(12) R. Pasternak, *Helv. Chim. Acta*, **31**, 753 (1958).

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

(14) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. II, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1952, p 684.

(15) Perone has reviewed the effects of varying per cents of alcohol in the polarography of benzophenone; *cf.*, S. P. Perone, "Kinetics and Mechanism of the Electroreduction of Benzophenone," University Microfilms, Inc., No. 64-602, Ann Arbor, Mich., 1963, pp 41 ff.

(16) The data presented by B. Gutbezahl and F. Grunwald [*J. Am. Chem. Soc.*, **75**, 559 (1953)] may be quoted in support of this assumption.

(17) A careful consideration of the extreme values in Table I suggests these ranges may be narrowed still further. The high value of 1.4 for the *dl/meso* ratio in run 1 may well be due to the uniquely long reaction time and the concomitant increase in alkalinity (final pH not recorded) which would tend to increase the ratio. If this run is not included, the range for the "acidic" media becomes 0.9–1.2. Further, the two lowest ratios recorded for alkaline runs (no. 8 and 14) describe those examples involving appreciably larger volumes of catholyte. It is reasonable to assume that the increases in alkalinity with time in these cases would be slower and the observed ratios somewhat lower. Exclusion of these two values leads to a ratio range of 2.7–3.2 for "alkaline" media. These several deletions would, accordingly, all reflect the difficulties of pH control.

TABLE I

ELECTROLYTIC BIMOLECULAR REDUCTION OF ACETOPHENONE-C^{14}

Run[a]	Electrode	Time, hr	Cathode potential/ current,[b] ma	Supporting electrolyte	Yield, % dl	Yield, % meso	Ratio dl/meso
			Acidic Media[c]				
1	Hg	53	−1.2/150 CP	LiCl	41.9	29.7	1.41
2	Hg	10	−1.1/200 CS	LiCl	23.2	24.8	0.93
3	Hg	20	−1.1/200 CC	LiCl	34.2	27.5	1.24
4	Sn	21	−1.1/500 CS	LiCl	29.6	28.7	1.03
5	Cu	21	−1.1/500 CS	LiCl	3.2	3.3	0.97
			Buffered Media				
6	Hg	10	−1.1/220 CS	KOAc[d]	18.8	19.0	0.98
7	Hg	20	−1.6/26 CP	NH_4OAc, NH_4OH[e]	24.4	21.8	1.11
			Basic Media[f]				
8	Hg	82	−1.6/70 CP	KOAc[g]	64.8	25.9	2.50
9	Hg	20	−1.6/30 CP	KOAc	30.1	9.5	3.15
10	Hg	20	−1.7/200 CC	KOAc	36.8	13.7	2.69
11	Hg	20	−1.7/200 CC	KOAc	39.1	12.7	3.07
12	Hg	42	−1.6/20 CC	KOAc	45.5	16.9	2.68
13	Hg	40	−1.6/20 CP	KOAc	44.8	15.7	2.85
14	Hg	20	−1.7/53 CP	KOAc[g]	52.6	21.8	2.47
15	Hg	20	−1.6/20 CC	KOAc, KOH[h]	48.0	14.9	3.22
16	Hg	20	−1.8/33 CP	Me_4NCl, Me_4NOH[i]	54.0	17.7	3.08
17	Hg	20	−1.6/26 CP	Me_4NOAc[j]	45.9	15.3	2.98
18	Sn	14	−1.6/400 CS	KOAc	41.2	14.5	2.88
19	Sn	12	−1.6/300 CS	KOAc	52.7	17.3	3.04
20	Cu	46	−1.5/200 CS	KOAc	51.6	20.7	2.77
21	Cu	10	−1.6/500 CS	KOAc, LiOH[k]	57.8	19.5	2.95
22	Cu	20	−1.5/200 CC	KOAc	57.8	20.4	2.83
23[l]	Hg	20	−/200 CC	KOAc	0	96.2	...

[a] Run number does not represent chronological order of experiment. [b] CP designates controlled potential (corresponding current is initial value), CC designates constant current (corresponding voltage is initial value), and CS designates uncontrolled DC rectifier power source (corresponding voltage and current are both initial values). [c] Solution 1.5 *M* in AcOH and 1 *M* in LiCl. Initial pH 4.2. See Experimental Section. [d] Solution 2.5 *M* in AcOH and 2 *M* in KOAc. Initial pH 6.5, did not rise above 7. [e] Solution 2 *M* in NH_4OAc and 1 *M* in NH_4OH. Initial pH 8.5, did not rise above 9. [f] Solution 2 *M* in KOAc unless otherwise specified. See Experimental Section. [g] Total cathode volume increased to approximately 250 cc. [h] Solution also 0.5 *M* in KOH. [i] No KOAc, solution 0.5 *M* in both Me_4NOH and Me_4NCl. [j] No KOAc, solution 1 *M* in Me_4NOAc. [k] Solution also 0.4 *M* in LiOH. [l] Product stability study; C^{14}-labeled *meso*-pinacol used; no reference electrode employed.

not appear to have a significant effect on the diastereomeric ratios observed.[18]

(f) The pinacolic products are not interconverted and are stable to the reaction conditions.

The conclusions have a number of important consequences.

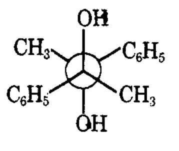
(1) From conclusion d above, the dimerization step probably does not occur on the electrode surface as has been suggested by some previous investigators.[19]

(2) The combining intermediates are clearly different in acidic and basic media. This point will be discussed in greater detail.

(3) The base stability of the acetophenone pinacols stands in marked contrast to that of the benzophenone analogs which are readily cleaved by strong base to benzhydrol and benzophenone, the latter to be recycled under the reaction conditions.[20] This latter cleavage proceeds rapidly enough to be of both synthetic[21] and analytical value.[22] Should the diastereomeric ratios be investigated in a monosubstituted benzophenone series, the point would assume considerable importance from both a yield basis as well as the likelihood of different rates of decay for the two diastereomers.

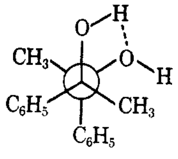
The formation of major amounts of pinacol under all conditions employed indicates that comparisons between the results obtained by different investigators must be made with considerable caution.[23]

Various investigators have suggested that the dimerizing species in acid solution is the free radical resulting from protonation of the carbonyl group and the transfer of one electron from the cathode.[13] Presuming the influence of the electrode surface at the time of dimerization to be negligible, one might predict that bond formation between dimerizing radicals would be more fruitful when the conformations A, B, and C resulted. A is formulated solely on steric grounds and B and C to permit intramolecular hydrogen bonding.



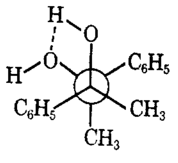
A

(yields *meso*)



B

(yields *dl*)



C

(yields *dl*)

The experimental results in Table I show that essentially equal amounts of the two diastereoisomers are produced in acidic solution. This leads to the conclusion that hydrogen bonding during carbon–carbon bond formation is of considerable importance.

This conclusion is further strengthened by an examination of the experimental results in basic media. Based on the general agreement that radical anions are produced by the transfer of a single electron to the carbonyl group when the electrolysis is carried out in alkaline media[13,24,25] and on the assumption that a substantial portion of these radical anions will abstract

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[18] These variables may have small but real effects on the stereochemistry under consideration. In view of the difficulties in experimental control where so large a number of variables may be interacting with one another, the authors prefer to take a conservative position.

[19] *E.g.*, (a) J. H. Brewster, *J. Am. Chem. Soc.*, **76**, 6361 (1965), and (b) M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958, p 48.

[20] It is quite possible that some of the benzhydrol reported as produced by the electrolytic reduction of benzophenone is, in fact, due instead to this subsequent cleavage of the pinacol in an increasingly alkaline media. The difference in stabilities of the two types of pinacols undoubtedly reflects the relative stabilities of the two intermediate anions, $(C_6H_5)_2(OH)C:^-$ and $(C_6H_5)(CH_3)(OH)C:^-$.

[21] W. E. Bachmann, *J. Am. Chem. Soc.*, **55**, 391 (1933).

[22] S. G. Cohen and J. I. Cohen, *ibid.*, **89**, 164 (1967).

[23] The difficulties of organizing the available data into a coherent whole are well illustrated by a careful reading of pp 61–66 of Allen's monograph[19b] and the important paper by Elving and Leone.[13] For example, Kolthoff and Lingane (ref 14, p 685) report that the product in acidic media is the pinacol and in basic media is the carbinol; Allen (ref 19b, p 64) reports the carbinol is obtained with a lower overpotential cathode while the pinacol required a higher overpotential electrode; Pasternak[12] claims predominately carbinol at pH 8 and reports its isolation; Elving and Leone[13] report the pinacol to predominate at low and high pH, reluctantly concluding on the basis of coulometric data that at an intermediate pH, specifically *ca.* 9, the carbinol is the primary product. Numerous other examples could be cited. While admittedly these various investigators employed somewhat different reaction conditions, notably media, the total picture is unsatisfactory. In general, the relative amounts of pinacol *vs.* carbinol, as reflecting the particular ketone and the unique reaction conditions, deserves a considerable amount of further study, not directly germane to the emphasis of the present investigation.

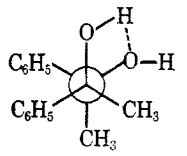
[24] S. Wawzonek and A. Gundersen, *J. Electrochem. Soc.*, **107**, 537 (1960).

[25] N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964). These investigators determined the esr spectra of acetophenone radical anions in an aparotic solvent.

a proton from any suitable source in the media, we are dealing with a mixture containing radicals as well as radical anions.

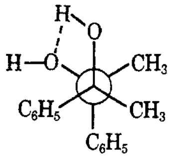
These two species may react in *three* different ways, *i.e.*, the combining of like species as well as cross-coupling.[26] The latter situation may be visualized by replacing one of the hydroxyl groups in A and the donor oxygen in B and C, with an oxygen anion, yielding the corresponding conformers at the time of coupling in alkaline media. The greatly enhanced production of the *dl* form would then follow from the increased preference of radical–radical anion conformations derived from B or C relative to A.

A fourth possibility, involving hydrogen bonding and leading to the *meso* form, could be formulated



D

or



D′

as D or D′. It will be noted that *either* formulation involves *both* nonbonded interactions—phenyl–phenyl *and* methyl–methyl. While a choice between B and C as to which of these interactions is least favorable cannot be made at this time, the fact that D possesses *both* has been deemed sufficient reason to consider its contribution a minimal one.

Run no. 7 (Table I) requires additional comment. Its diastereomer ratio of 1.11 places it clearly with those in the "acid" range although it was carried out at a relative pH of 8.5 in buffered media. All "alkaline" runs may be assumed to have been carried out at pH value of 11 or higher.[27] Clearly a greater concentration of hydroxide ions than were available at pH values of 8.5–9 are necessary to prevent essentially complete protonation of any radical anions produced and pinacol formation from solely radical combination.

Further work is currently under way involving both the benzaldehyde and propiophenone systems. The data to be derived from this research should provide a more extensive test of the proposed mechanism.

The research reported here has practical applications. The *dl* form of acetophenone pinacol may be prepared synthetically, in competitive yield, by the electrolytic reduction of the ketone in alkaline media. Specialized equipment (reference electrode, controlled potential, etc.) is not required.

Experimental Section

The routine chemicals employed were either reagent grade or the best research grade obtainable and were used as received. Acetophenone-7-C^{14} was purchased from Nuclear Research Chemicals, Orlando, Fla., and diluted with Eastman White Label material to suitable levels of activity. *meso*-2,3-Diphenyl-2,3-butanediol (mp 120–121°) was prepared by the stereoselective addition of methyllithium to benzil; the *dl* form (mp 125–126°) was similarly prepared by the addition of phenyllithium to freshly distilled biacetyl. C^{14}-labeled *meso*-pinacol was prepared correspondingly from labeled benzil.[1a] Radioactivity was measured on a Tri-Carb scintillation counter (Packard Instrument Co., Inc.). Melting points were determined on a Kofler hot stage and are uncorrected.

Experimental Design.—The earlier studies were carried out employing an Analytical Instrument Co. potentiostat and coupled current integrator. Subsequently, a specially designed, inexpensive, transistorized analog, capable of both controlled-potential and constant-current operation, evolved through several modifications and was employed in the bulk of the runs. Various cells were used including standard three-compartment cells with sintered-glass separations, and simple porous cup anode compartments set in large beakers containing the cathodes. *Because the experimental design did not appear to have any significant effect on the diastereomeric ratios observed* (see Table I), no elaboration of the above will be reported here.[28]

Representative Procedure.—(Hg cathode, controlled potential, beaker–porous cup cell, see Table I, item 13). A 1-cm length of platinum wire sealed through the side at the base of a 250-ml beaker into a 8-cm length of 7-mm diameter glass tubing permitted electrical contact between the pool of mercury at the bottom of the beaker (area approximately 150 cm^2) serving as the cathode and the added mercury in the side arm. A porous cup (battery type, Coors No. 1) inserted through a no. 13 rubber stopper fitted into the beaker served as an anode compartment. The anode was a platinum wire; the anode electrolyte was 1 *M* aqueous lithium nitrate. The rubber stopper was also bored to accommodate a gas-dispersion tube, a thermometer, and a calomel reference electrode (Beckman No. 39005, containing a saturated lithium chloride salt bridge in place of potassium chloride), which was placed as close to the mercury pool as possible. The cell contents were stirred magnetically and the anode compartment was placed to minimize electrode distances. Dry nitrogen was bubbled through both compartments; it was passed through an 80% ethanol solution prior to bubbling through the cathode compartment only.

A solution of 1.0088 g of acetophenone-7-C^{14} (3953 dpm/mg) in 60 cc of 80% ethanol that was 2.0 *M* with respect to potassium acetate was placed in the cell and electrolyzed under conditions of controlled potential (-1.6 v relative to the calomel electrode) at an initial current of 20 ma for 40 hr. The cathode contents were then transferred quantitatively by decantation and thorough rinsing of all pertinent surfaces into a 100-cc volumetric flask. After dilution to the mark with methanol, a 50-cc aliquot was pipeted into an Erlenmeyer flask containing 0.9409 g of pure, unlabeled *meso*-pinacol and the remaining 50 cc was transferred quantitatively into a second flask containing 1.0453 g of pure, unlabeled *dl*-pinacol. The solutions in the individual flasks were concentrated on a steam bath with an air stream to the point of essentially complete removal of alcohol and the remaining material was well extracted with hot heptane. Cooling yielded the isolated pinacol. Four to six recrystallizations from heptane usually ensured the pure diastereomer. Radioassay[29] of 10–15-mg samples gave activities of 312.1 dpm/mg for the *meso* product and 709.2 dpm/mg for the racemate, calculating to a yield of 15.74% *meso* and 44.81% racemate and a racemate/*meso* ratio of 2.85. Results from and variations in the above general procedure are noted in Table I.

Registry No.—*meso*-2,3-Diphenyl-2,3-butanediol, 4217-65-6; *dl*-2,3-diphenyl-2,3-butanediol, 5132-85-4; acetophenone-7-C^{14}, 98-86-2.

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(26) Elving and Leone[13] have proposed a similar interaction of radical anions with media to produce radicals. They postulate pinacol formation may take place from the dimerizing of either the radical or the radical anion, but do not consider the coupling of the *two different species* proposed here. The changed stereochemistry from that observed in acid media clearly indicates that radical–radical coupling is *not* the predominate route in alkaline media while the dimerization of two negatively charged species is both electrostatically unattractive as well as producing preferentially, on polarity grounds, the *meso* form. This point will be investigated further by utilizing aprotic media.

(27) See earlier comments about pH control.

(28) Circuitry and specifications of the transistorized analog, to be used with standard dc power sources, will be submitted to a suitable journal. The authors will be pleased to answer any inquiries.

(29) A brief but useful review of the principles and practice of isotope dilution techniques may be found in G. D. Chase and J. L. Rabinowitz, "Principles of Radioisotope Methodology," 2nd ed, Burgess Publishing Co., Minneapolis, Minn., 1962, pp 281ff.