step process. It further indicates that more than one route is involved in pinacol formation.

If it is argued that the ketyl radical III is the intermediate reduced to carbinol at higher pH's, an active role must be assigned to anion II. Then the combination of II and III (route C), in the presence of decreased amounts of III due to its loss to form carbinol, could be increasingly important and account for the higher *dl/meso* ratios. Thus, the high current, the more negative potentials on the mercury electrodes, and the appreciably more negative potentials observed with the copper electrodes would all represent the same phenomena: an increasing ease of reduction of III to carbinol, a consequent decrease in dimerization of III, and an increase in the combination of II with III. The above presupposes that the solution equilibria involved must be slow enough to be effectively disturbed by the withdrawal of some constituent; there would otherwise be no change in the stereoselectivity observed.

It may be added that the controlled potential reduction of 2-acetylpyridine should be considered attractive for the synthesis of preparative scale amounts of the carbinol and the *meso*-pinacol, the former in strongly acidic media and the latter in alkaline media at moderate current levels.

Experimental Section

The routine chemicals employed were either reagent grade or the best research grade obtainable and were further purified by conventional techniques where necessary.

The general procedure has been reported in detail.[1,2,14] All runs involved 1 g of ketone in 60 ml of solution. Modifications in the general procedure are described in Table I. *dl/meso* ratios were determined by a comparison of peak heights of the methyl groups of the two diastereomers. Yields were based on a comparison, after normalization, of the integrated area of the methyl groups with the total aromatic area. Recovered ketone was evaluated similarly.

***meso*-2,3-Di(2-pyridyl)-2,3-butanediol.**—This material was isolated by simple crystallization from reaction mixtures corresponding to item 16 in Table I (2 *M* KOAc, 80% EtOH, −1.15 V, and initial current 600 mA). Two recrystallizations from hot heptane yielded chunky white crystals, mp 142–143°. Photochemical bimolecular reduction of 2-acetylpyridine was also employed.[6]

***dl*-2,3-Di(2-pyridyl)-2,3-butanediol.**—A modification of the procedure reported by Bencze and Allen[6] was employed. To an ether solution of methylmagnesium iodide (from 0.25 mol of Mg and 0.25 mol of CH_3I) was added 12.1 g (0.06 mol) of α-pyridil. Following an 18-hr reflux and conventional work-up, 7.9 g of *dl*-pinacol (55%), mp 139–140°, was isolated. Two recrystallizations from hexane yielded fine needle crystals, mp 142°.

Registry No.—2-Acetylpyridine, 1122-62-9; methyl-2-pyridylcarbinol, 18728-61-5; *meso*-2,3-di(2-pyridyl)-2,3-butanediol, 20445-38-9; *dl*-2,3-di(2-pyridyl)-2,3-butanediol, 20445-39-0.

Acknowledgment.—Financial support from the U. S. Atomic Energy Commission under Contract AT-(40-1)-2833 (ORO-2833-21) is gratefully acknowledged. The nmr instrument utilized, an A-60 (Varian Corp.), was awarded to Louisiana State University in New Orleans by the National Science Foundation under Grant GP-3674.

(14) A Ag/AgCl reference electrode was used in place of the previously employed standard calomel electrode. As used with saturated KCl, it is 0.04 V more negative than the latter.

Quantitative Studies in Stereochemistry. Photochemistry. VII. Electrochemistry. IV. The Photochemical and Electrochemical Bimolecular Reduction of Aldehydes and Unsymmetrical Ketones; a Common Stereochemistry[1]

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New and previously published data in the two title areas are tabulated and the stereochemical results from the two techniques are compared. In all cases, both photochemical and electrochemical pinacolizations gave essentially the same ratios of diastereomeric *dl*- to *meso*-pinacols in acid solution with corresponding changes of ratios in basic media. Mechanisms previously proposed for the photochemical and the electrochemical routes are shown to be mutually compatible. Several examples of contrasting behavior, *i.e.*, successful pinacolization by only one of the two techniques, are reported and discussed.

A number of papers from this laboratory have reported the *dl/meso* ratios of diastereomeric pinacols formed in the photochemical[2-7] and electrochemical[8-10] bimolecular reduction of benzaldehyde and unsymmetrical ketones. As the roughly parallel studies in the two areas progressed, it became increasingly apparent that the diastereomeric ratios observed could only be explained by the two techniques sharing a common mechanism at some terminal point. This present report brings together data from all previous papers, selected to facilitate comparisons, with additional unpublished

(1) Presented in part before the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966). (Acetophenone in neutral and acid media)

(3) J. H. Stocker and D. H. Kern, *ibid.*, **33**, 291 (1968). (Acetophenone in basic media; benzaldehyde)

(4) J. H. Stocker, D. H. Kern, and R. M. Jenevein, *ibid.*, **33**, 412 (1968). (*p*-Substituted acetophenones)

(5) J. H. Stocker and D. H. Kern, *ibid.*, **33**, 1270 (1968). (Acetophenone in amine media)

(6) J. H. Stocker and D. H. Kern, *ibid.*, **33**, 1271 (1968). (Deoxybenzoin)

(7) J. H. Stocker and D. H. Kern, submitted for publication in *J. Org. Chem.* (2-Acetylpyridine)

(8) J. H. Stocker and R. M. Jenevein, *J. Org. Chem.*, **33**, 294 (1968). (Acetophenone)

(9) J. H. Stocker and R. M. Jenevein, *ibid.*, **33**, 2145 (1968). (Benzaldehyde and propiophenone)

(10) J. H. Stocker and R. M. Jenevein, *ibid.*, **34**, 2807 (1969). (2-Acetylpyridine)

information that permits a maximum number of cross correlations. The only variable common to the two techniques that was demonstrated to have a major effect on the stereochemistry was pH; the data, accordingly, have been grouped in such a way as to reflect this. The new data appear in Table I; the summary tabulation appears in Table II.

TABLE I

PINACOLIZATION OF SUBSTITUTED ACETOPHENONES[a]

Item	Technique[b]	Time, hr	Pinacol,[c] %	Ratio of *dl*/*meso*	Modifications
			Propiophenone[d]		
1	P	2	7.4	1.34	1 drop AcOH added
2	P	18	63.9	1.24	1 drop AcOH added
3	P	30	91.1	1.23	1 drop AcOH added
4	P	18	45.2	1.45	50% aq
5	P	18	36.0	2.13	50% aq, soln 0.01 *N* in KOH
6	P	18	26.1	2.98	50% aq, soln 0.2 *N* in KOH
7	P	72	70.2	2.17	Same as 6
8	P	18	31.9	3.10	50% aq, soln 0.5 *N* in KOH
9	P	72	(98.0% *dl*, 0% *meso*)		Pure *dl*-pinacol as starting material, 50% aq, soln 0.2 *N* KOH
			p-Chloroacetophenone[e]		
10	P	24	23	2.92	Basic, see 6
11	P	48	30	2.22	Basic, see 6
12	E	3	88	1.18	Soln 1.7 *M* in AcOH, 1.0 *M* in LiCl, −1.1 V, 200 mA[f]
13	E	4	95	3.08	Soln 0.2 *M* in KOAc, −1.7 V, 410 mA[f]
			p-Methoxyacetophenone[g]		
14	P	168	26	2.25	Basic, see 6
15	E	9	96	1.24	Acidic, see 12, −1.2 V, 500 mA[f]
16	E	4	96	3.03	Basic, see 13, −1.7 V, 300 mA[f]
			p-Trifluoromethylacetophenone[e]		
17	E	1	87	1.02	Acidic, see 12, −1.2 V, 490 mA[f]
			Deoxybenzoin[g]		
18	E	1.5	44	1.33	Acidic see 12, −1.2 V, 530 mA[f]
19	E	3	98	3.20	Basic, see 13, −1.4 V, 410 mA[f]

[a] Previously unpublished. [b] P = photochemical, absolute 2-propanol solvent; E = electrochemical, Hg pool electrode, 80% ethanol solvent. [c] Based on starting ketone. [d] Isotope dilution studies utilizing propiophenone-7-^{14}C; see ref 9. [e] Nmr analysis; see ref 4. [f] Controlled potential, initial current. [g] Nmr analysis; see ref 6.

Results and Discussion[11]

A careful examination of the tabulated ratios in Table II suggests that they may be divided conveniently into three categories: (a) benzaldehyde; (b) acetylpyridine; and (c) "acetophenones," both ring and side-chain substituted. The latter category has been studied the most extensively, and the results permit

(11) Much of this discussion has appeared in previous papers,[3-10] *each dealing solely with electrochemical or photochemical studies.* Some repetition will be necessary to place the results in a larger framework. Reference to earlier papers may be made for more detailed treatment of individual cases.

TABLE II

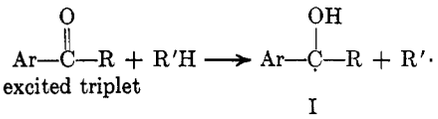
SUMMARY TABULATION OF BIMOLECULAR REDUCTION OF ArCOR

Item	Technique[a]	*dl*/*meso* ratios[b,c] Acidic media	Basic media
	Ar = C_6H_5, R = H (Benzaldehyde)		
1	P	1.01–1.03[d]	1.15–1.20[d]
2	E	1.1[e]	1.18–1.20[e]
	Ar = C_6H_5, R = CH_3 (Acetophenone)		
3	P	1.06–1.14[f]	2.37–3.20[g]
4	E	0.93–1.41[h]	2.47–3.20[h]
	Ar = C_6H_5, R = C_2H_5 (Propiophenone)		
5	P	1.23–1.34	2.98–3.10
6	E	1.40–1.42[i]	2.67–3.05[i]
	Ar = *p*-ClC_6H_4, R = CH_3 (*p*-Chloroacetophenone)		
7	P	1.1[j]	2.9
8	E	1.2	3.1
	Ar = *p*-$CH_3OC_6H_4$, R = CH_3 (*p*-Methoxyacetophenone)		
9	P	1.3[j]	2.3
10	E	1.2	2.9
	Ar = *p*-$CF_3C_6H_4$, R = CH_3 (*p*-Trifluoromethylacetophenone)		
11	P	0.95–0.98[j]	...[k]
12	E	1.0	...[k]
	Ar = C_6H_5, R = $C_6H_5CH_2$ (Deoxybenzoin)		
13	P	1.15[l]	3.0[l]
14	E	1.3	3.2
	Ar = 2-Pyridyl, R = CH_3 (2-Acetylpyridine)		
15	P	0.78–0.98[m]	0.62–0.65[m]
16	E	0.73–0.78[n]	0.22–0.28[n]

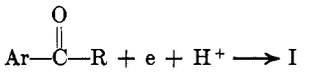
[a] P = photochemical, E = electrochemical. [b] Results from a single run are expressed to the nearest tenth; all other ratios involve 2–12 runs and have been expressed as ranges. [c] Photochemical ratios reported for acid media involve only absolute 2-propanol solvent; in basic media both absolute and 50% aqueous 2-propanol results are included. All electrochemical ratios reported were determined in 80% ethanol and are limited to those runs involving a maximum current of 500 mA or less. [d] From ref 3. [e] From ref 9. [f] From ref 2. [g] From ref 3. [h] From ref 8. [i] From ref 9. [j] From ref 4. [k] Ketone is consumed; no pinacol produced. [l] From ref 6. [m] From ref 7. [n] From ref 10.

somewhat more satisfactory conclusions. After the following general comments, the several categories will be treated individually.

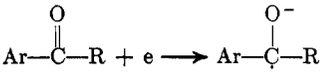
General.—It is generally accepted that the ketyl radical I is produced both photochemically and electrochemically as follows:



I



Further, it appears well established that the radical anion II is produced electrochemically under "basic" or aprotic conditions.



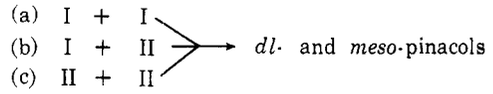
II

Successful photopinacolizations in basic media lead us to suggest that the following equilibrium is involved,

$$I + OB^- \rightleftharpoons II + BOH$$

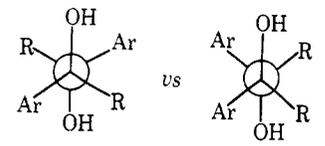
(B = H, alkyl)

both photochemically and electrochemically, the relative amounts of I and II reflecting the amount and strength of added base. Accordingly, *three* possible combinations leading to pinacol have to be considered.



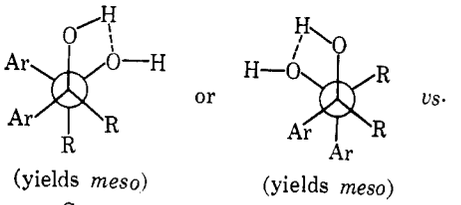
Combination a would be expected to predominate in acid media; combination c would be rejected on the basis of electrostatic repulsion between like-charged species; and combination b would then be expected to make a major contribution in alkaline media. *The following discussion refers interchangeably to both the photochemical and electrochemical techniques.*

Acetophenones.—Perhaps the two most obvious factors that might be expected to exercise stereochemical control of bond formation between species about to combine are the simple steric and the hydrogen bonding. The former would lead to the prediction of a predominance of the *meso* form from A, the *only* possible conformation at the time of bond formation that has *no*

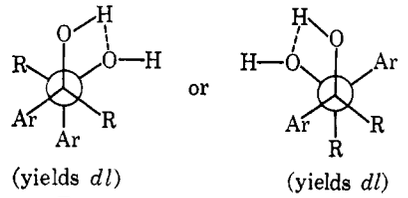


(yields *meso*) A (yields *dl*) B

nonbonded interactions between like groups. *All* other possibilities leading to either diastereomer have one or two such interactions, for example, B. Interspecies hydrogen bonding, however, would appear to favor the *dl* form; a comparison of C or D, each with two nonbonded interactions, with E or F, each with only one, illustrates this.

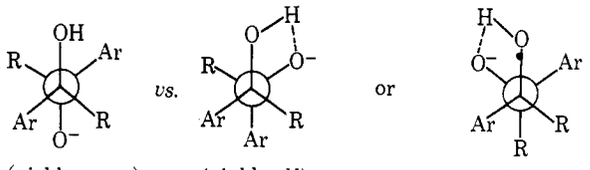


(yields *meso*) C (yields *meso*) D



(yields *dl*) E (yields *dl*) F

The above considerations, in light of the observed slight predominance of the *dl* form for acetophenones in neutral and acidic media, lead to the conclusion that hydrogen bonding is not only important but plays a decisive role. This viewpoint is further strengthened by an examination of the results in alkaline media. Here we have the possibility of hydrogen bridging *via* the anionic oxygen of the radical anion; and the earlier comparison of E or F, producing *dl*, with A, producing *meso*, now becomes a contrasting of H or I with G.



(yields *meso*) G (yields *dl*) H (yields *dl*) I

The greater strength of hydrogen bonding should be reflected in an increased preference for H or I relative to G. This increased preference would be reflected in a sharply increased *dl/meso* ratio.[12]

In choosing between E (aryl–aryl interactions) and F (alkyl–alkyl interactions), it is pertinent to note that there is a definite increase in the *dl/meso* ratios in acid solution as the alkyl group goes from methyl to benzyl or ethyl. This increase would support the assignment of a greater "effective bulk" to methyl than to phenyl and would lead to the series ethyl ≅ benzyl > methyl > phenyl. Expressed in another way, if the aryl group interactions were the more controlling (*i.e.*, E), the *dl/meso* ratios should *decrease* as the alkyl group grew more bulky.[13]

This evaluation receives additional support from certain nmr data. Measurement of the separation of the hydroxylic proton resonance frequencies of the two diastereomers of each pinacol in dilute solution should reflect the relative degree of *intra*molecular hydrogen bonding. The greater the separation in any one pair of diastereomers, the more effectively internally bound the *dl* form (the more deshielded form in all cases) must be. The pertinent figures ($\Delta\ \tau$) are 0.32 for the acetophenone pinacols, 0.46 for the propiophenone pinacols, and 0.61 for the deoxybenzoin pinacols. These figures indicate an increasing amount of intramolecular hydrogen bonding in the *dl* form, relative to the *meso*, with increasing alkyl "size" and strongly suggest control by E (and, by implication, H) of the resultant stereochemistry.

Benzaldehyde.—The diastereomer ratios reported for benzaldehyde show only a very slight stereoselectivity in either acid or base. While it is possible to consider the results as arising from competition between steric control and hydrogen bonding, with hydrogen and phenyl groups interacting, it seems considerably more reasonable to assume simply that hydrogen interactions at the time of coupling may be permitted and the less favorable conformations rejected, for the acetophenones play a greater role. It is further possible that the benzaldehyde ketyl radical and radical anion are simply more reactive than their acetophenone counterparts and hence less discriminating.[14]

These interpretations would lead to the prediction that all aromatic aldehydes would be expected to

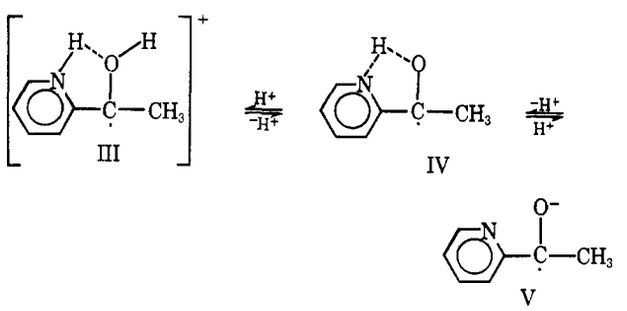
(12) For some comments about the relative fraction of the reaction proceeding through (a) radical dimerization and (b) radical coupling with radical anion, see ref 3, footnote 10.

(13) Preliminary data from cyclohexyl phenyl ketone (electrochemical only) and *ortho*-substituted acetophenones support this viewpoint. The former shows a *dl/meso* ratio greater than 1.5:1 in acid media and the latter show sharply *reduced* (compared with acetophenone) ratios in alkaline media.

(14) Some stability data from esr studies support this possibility; *i.e.*, N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).

display negligible stereoselectivity.[15] What is more germane to this report is, however, that, irrespective of the correctness of this prediction, whatever conclusions are drawn should apply equally satisfactorily to the stereochemistry of both the photochemical and the electrochemical bimolecular reductions.

2-Acetylpyridine.—The results for 2-acetylpyridine require some additional comment. The important intermediates to be considered would be the following.



III IV V

Rejecting any important contribution from the dimerization of charged species III and IV, and assuming that the concentration of V, a rather strong base, will be very small in any protic media, there is left only the dimerization of IV and the coupling of III and IV.

The dimerization of IV would not involve *inter*species hydrogen bonding and would be subject to simple steric control. It should yield predominantly the *meso* form by analogy with the acetophenone systems and would constitute the major pathway. The coupling of III and IV, with possible *inter*species hydrogen bridging, should favor formtion of the *dl* form. To the extent that this coupling makes a contribution in increasingly acid solution, the *dl*/*meso* ratios of pinacols should less favor the *meso* form. Accordingly, for both the electrochemical and photochemical techniques, we would find predominantly the *meso* form, with the highest *dl*/*meso* ratios observed in strong acid and the lowest in strong base.[16,17]

Contrasts between the Two Techniques.—It must be kept in mind that *only* the *final* step in the photopinacolization and electropinacolization reactions is under consideration. The two techniques have very different mechanisms prior to this step, and *only those compounds successfully pinacolized by both techniques can be compared.* Any alternate pathways available to any intermediate and unique to that particular technique would make hypothetical predictions of the expected stereochemistry meaningless. Some specific examples of "unsuccessful" pinacolizations by only one of the two techniques have been observed in this laboratory and are tabulated in Table III. The unsuccessful photopinacolizations of benzaldehyde and 2-acetylpyridine in strong base (>0.1 *N* KOH) are due to an as yet undetermined uv-accelerated alternate reaction. Phenyl cyclohexyl ketone, in turn, photopinacolizes so slowly that alternative cleavage reactions are more rapid and take precedence.[18] Electrochemically, 2-acetylpyridine proceeds so overwhelmingly to the carbinol in strongly acidic media that its pinacolization should be classed as a failure.

Electrochemical failure of the trifluoro ketone to pinacolize is due to complete C–F fission at a potential lower than that required for pinacolization.[19]

TABLE III
CONTRASTS IN PHOTO- AND ELECTROPINACOLIZATION

	Photochemical	Electrochemical
Benzaldehyde	Unsuccessful in strong base	Successful in strong base
α,α,α-Trifluoroacetophenone	Successful in acid	Unsuccessful in acid
2-Acetylpyridine	(a) unsuccessful in strong base (b) successful in strong acid	(a) successful in strong base (b) unsuccessful in strong acid
Phenyl cyclohexyl ketone	Unsuccessful	Successful

Experimental Section

The general procedures and the specialized apparatus employed in the isotope dilution studies have been previously described (electrochemical,[8] photochemical[2]). Alterations in the general procedures to permit nmr analysis have also been reported.[4,9,10] Sources of materials for previously unreported studies may be cross referenced in Table II, *e.g.*, the propiophenone-7-^{14}C and its related pinacols utilized in the photochemical studies are described in the indicated reference to the electrochemical analogs.

Registry No.—Propiophenone, 93-55-0; *p*-chloroacetophenone, 99-91-2; *p*-methoxyacetophenone, 100-06-1; *p*-trifluoromethylacetophenone, 709-63-7; deoxybenzoin, 451-40-1.

Acknowledgment.—Financial support of this research under Atomic Energy Contract AT-(40-1)-2833 (ORD-2833-22) is gratefully acknowledged. The nmr instrument employed, an A-60 (Varian Corp.), was awarded to Louisiana State University in New Orleans by the National Science Foundation under GP-3674.

(15) The electrochemical bimolecular reduction of *p*-hydroxybenzaldehyde [J. Grimshaw and J. S. Ramsay, *J. Chem. Soc., C*, 653 (1964)] in alkaline aqueous media constitutes a known contradiction to this prediction; an 85% crude yield of the *meso*-hydrobenzoin was isolated with none of the *dl* form reported. This is, however, a rather special case involving a charged aldehyde; *i.e.*, the phenoxide form is undoubtedly involved.

(16) This analysis is admittedly an oversimplification. The 2-acetylpyridine system has proved to be a very "sensitive" system, in contrast to acetophenones which are relatively "insensitive." The individual photochemical and electrochemical results from 2-acetylpyridine are treated in much greater depth in ref 7 and 10, respectively. It should perhaps be emphasized, once again, that results from the various systems by each of the two techniques have been selected to facilitate comparisons.

(17) There is a disparity in the electrochemical and photochemical results for 2-acetylpyridine not found in the other systems. The displacement of the *dl*/*meso* ratios to lower values in the electrochemical studies can be explained by invoking III as the precursor to the methyl-2-pyridylcarbinol observed only in the electrochemical runs. This monomolecular reduction product is the predominant one in acid media; and its production, other factors being constant, is directly proportional to the acidity. To the extent that III is removed to form carbinol, the combination of III and IV is diminished and *dl*/*meso* ratios are decreased in the electrochemical studies.

(18) J. H. Stocker and D. H. Kern, *Chem. Comm.*, 204 (1969).

(19) J. H. Stocker and R. M. Jenevein, *ibid.*, 934 (1968).