Monofluoroacetylene is known to decompose at its boiling point.[20] As a consequence of this, yields of 1-fluorovinyl bromide, bp 6–8° (lit.[21] bp 6.8°) varied considerably in successive runs (20–45%). Attempts to repeat the experiment in mineral oil gave similar results and no 1-fluorovinyl bromide was obtained from the reaction carried out in ethanol.

The preparation and reaction of 1-fluorovinyllithium were then carried out in a manner similar to that described previously for 2,2-difluorovinyllithium.

Registry No.—1, 15051-86-2; 1 S-benzylisothiuronium salt, 15051-85-1; 2, 1869-14-3; 3, 15051-83-9; 4, 708-84-9; 5, 15052-21-8; 6, 430-99-9; 7, 2365-87-9; 7 *p*-nitrobenzyl ester, 15156-69-1; 8, 15052-24-1; 9, 350-90-3; 9 S-benzylisothiuronium salt, 15052-26-3; 11, 15052-92-3; 12 S-benzylisothiuronium salt, 15053-97-1; 13, 15052-93-4; 14, 15052-94-5; 15, 15053-98-2; 16, 1727-39-5; 17, 625-23-0; 18, 541-47-9; 20, 1552-91-6; 20 S-benzylisothiuronium salt, 15052-99-0; 21, 5851-65-0; 22, 15053-01-7.

Acknowledgment.—This work was carried out under Research Contract No. DA19-129-AMC-79(N) sponsored by the U. S. Army (Natick) Laboratories where Mr. C. B. Griffis was scientific officer. We are also grateful to Dr. R. S. Brey for nmr analyses.

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(20) W. J. Middleton and W. H. Sharkey, *J. Am. Chem. Soc.*, **81**, 803 (1959).

(21) F. Swartz, *Bull. Acad. Roy. Belg.*, 563 (1911).

Quantitative Studies in Stereochemistry. B. Photochemistry. II. Solvent and Basicity Effects on the Ratio of Diastereomeric Glycols Formed in the Ultraviolet-Promoted Bimolecular Reduction of Acetophenone-7-C^{14} and Benzaldehyde-7-C^{14}

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Substitution of various media for the 2-propanol customarily employed in the photopinacolization of acetophenone produced small but real changes in the ratio of *dl*/*meso* diastereomers formed. Values from 1.03 (cyclohexane) to 1.31 (50% aqueous 2-PrOH) were observed. In the presence of strong base in 2-propanol, *dl*/*meso* ratios as high as 3:1 were found. It is proposed that the more stereoselective reactions in base result from the combination of radical anions with ketyl radicals. The *dl*/*meso* ratios for benzaldehyde were observed to be lower than those for acetophenone under identical reaction conditions. The glycols proved stable to the strongly alkaline reaction conditions.

A recent report[1] from this laboratory described the ratio of diastereomeric acetophenone pinacols resulting from the ultraviolet irradiation of acetophenone-7-C^{14} in slightly acidic 2-propanol. Employing wavelengths above 3000 A, a remarkably constant predominance of the *dl*-pinacol over the *meso* form in an 11:10 ratio was observed irrespective of time, concentration of ketone, intensity of radiation, and degassing.

The possibility of carrying out the pinacolization reaction in other than neutral or slightly acidic media was not seriously considered during the early part of the investigation; strongly acidic media might induce the pinacols present to rearrange, while alkaline media are routinely avoided in photopinacolizations to the point of adding sufficient acid to insure nonbasicity. This latter practice derives from reports by Bachmann[2,3] that the pinacol derived from benzophenone cleaved in alkaline media to benzhydrol plus regenerated ketone rapidly and in sufficiently good yield to make the method of synthetic value. This report has been confirmed with a change in mechanism by Cohen and Sherman[4] who have utilized this reaction for analytical purposes.[5] Data are hereby offered to indicate that the pinacolization of acetophenone does indeed occur in basic as well as acidic media but with quite different stereochemical consequences.

To provide some significant comparisons, the stereochemistry of the photochemical bimolecular reduction of benzaldehyde was also studied. The use of this system was designed to permit a comparison of the relative importance of the methyl group in acetophenone with the aldehydic hydrogen in benzaldehyde in determining the resultant stereochemistry. This system lent itself well to examination; the labeled aldehyde was commercially available, the diastereomeric hydrobenzoins were conveniently accessible by standard synthetic techniques (see Experimental Section), and their identities have been satisfactorily established.[6]

Additional stereochemical information was obtained from selected variations in temperature and the composition of the solvent/donor. The stabilities of the pinacols and glycols were also examined.

Results and Discussion

The *dl*/*meso* ratios of diastereomers formed are tabulated in Table I. It is probably most convenient to examine the stereochemistry of the acetophenone system first. The data may be divided into two distinct ranges, 1.0 to 1.3 and above 2.4. Most significant is the high stereoselectivity arising from the use of strong bases in the reaction media. The authors would like to propose that a radical anion II results from base attack upon the ketyl radical I,[1] reaction 1.

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(1) J. H. Stocker and D. H. Kern, *J. Org. Chem.*, **31**, 3755 (1966).

(2) W. E. Bachmann, *J. Am. Chem. Soc.*, **55**, 391 (1933).

(3) W. E. Bachman, *Org. Syn.*, **2**, 71 (1943).

(4) S. G. Cohen and W. V. Sherman, *J. Am. Chem. Soc.*, **85**, 1642 (1963).

(5) S. G. Cohen and J. I. Cohen, *ibid.*, **89**, 164 (1967).

(6) G. Berti and F. Bottari, *J. Org. Chem.*, **25**, 1286 (1960).

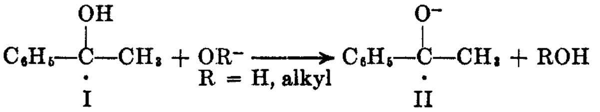
Table I

Irradiation of Acetophenone-C^{14} and Benzaldehyde-C^{14}

Run no.[a]	Solvent/donor	Time, hr	Products[b] % *dl*	Products[b] % *meso*	Ratio *dl*/*meso*[c]	Modifications[d]
				Acetophenone		
1[e]	2-PrOH	18	52.2	48.1	1.08	Standard run for reference
2[e]	2-PrOH	8	52.7	46.7	1.13	Standard run for reference
3	2-PrOH	18	41.0	35.8	1.14	10% trifluoroacetic acid present
4	EtOH	18	25.0	22.8	1.09	20% aqueous
5	2-PrOH	18	53.7	40.9	1.31	50% aqueous
6	2-Pentanol	18	42.4	40.5	1.04	
7	2-Pentanol	18	32.3	31.1	1.03	Reflux temperature (120°)
8[e]	Cyclohexane	18	4.4	4.2	1.05	
9	Cyclohexane	72	17.0	16.5	1.03	0.5 g ketone in 5 ml of solvent
10	2-PrOH	18	47.1	42.3	1.11	10% pyridine present
11	2-PrOH	18	41.3	29.2	1.41	Solvent 0.001 *N* in potassium 2-propoxide
12	2-PrOH	18	42.3	14.1	2.98	Solvent 0.01 *N* in potassium 2-propoxide
13	2-PrOH	18	34.7	10.8	3.20	Duplicate run to no. 12
14	2-PrOH	18	39.9	15.5	2.56	Solvent 0.2 *N* in potassium 2-propoxide
15	2-PrOH	42	44.3	18.6	2.37	Duplicate run to no. 14, longer time
16	2-PrOH	18	16.1	6.6	2.44	Solvent 1 *N* in potassium 2-propoxide
17	2-PrOH	18	26.3	12.5	2.10	50% aqueous, solvent 0.01 *N* in KOH
18	2-PrOH	18	27.9	9.8	2.85	50% aqueous, solvent 0.2 *N* in KOH
19	2-PrOH	18	56.8	23.6	2.41	Solvent 0.2 *N* in KOH
20	2-PrOH	72	2.2	94.0	. . .	1 g of pure *meso* pinacol starting material, solvent 0.2 *N* in potassium 2-propoxide
				Benzaldehyde		
21	2-PrOH	18	40.7	39.4	1.03	
22	2-PrOH	2	8.9	8.8	1.01	
23	2-PrOH	18	19.8	16.2	1.22	50% aqueous
24	2-PrOH	18	27.0	23.3	1.15	50% aqueous, solvent 0.01 *N* in KOH
25	2-PrOH	18	31.1	26.6	1.20	See run 24, 250 ml of solvent, 0.5 g of aldehyde
26	2-PrOH	70	<1	<1	. . .	35 ml of solvent, 50% aqueous, solvent 0.08 *N* in KOH
27	2-PrOH	18	<1	<1	. . .	50 ml of solvent, solvent 0.01 *N* in potassium 2-propoxide
28	2-PrOH	18	<1	<1	. . .	Solvent 0.2 *N* in potassium 2-propoxide
29	2-PrOH	24	2.7	95.8	. . .	0.5 g of pure *meso* (5%) as starting material, solvent 0.2 *N* in potassium 2-propoxide

[a] Designation of run number does not represent chronological order of experiment. [b] Per cent yields are based on starting ketone or aldehyde. [c] Reproducibility: run no. 1 may be reported as 1.085 ± 0.013. See ref 1. [d] Variations in the general procedure described in the Experimental Section. [e] From ref. 1.

Three modes of dimerization are then possible, reactions 2, 3, or 4.



$$\underset{\text{I}}{C_6H_5\text{—}\overset{\overset{\text{OH}}{|}}{\underset{\bullet}{C}}\text{—}CH_3} + \underset{R\,=\,H,\ \text{alkyl}}{OR^-} \longrightarrow \underset{\text{II}}{C_6H_5\text{—}\overset{\overset{O^-}{|}}{\underset{\bullet}{C}}\text{—}CH_3} + ROH \qquad (1)$$

$$\text{I} + \text{I} \rightarrow \underset{\text{III}}{\textit{meso}} \text{ and } \underset{\text{IV}}{\textit{dl}} \text{ pinacol} \qquad (2)$$

$$\text{I} + \text{II} \xrightarrow{H^+} \text{III} + \text{IV} \qquad (3)$$

$$\text{II} + \text{II} \xrightarrow{2H^+} \text{III} + \text{IV} \qquad (4)$$

In all solutions of insufficient base strength to abstract the hydroxylic proton from I, the dimerization of radical I *via* pathway 2 to produce the observed pinacols prevails. Such a situation obtains in runs 1–10 in Table I. Beginning with run 11, conditions permit a sufficient concentration of II[7–9] to be formed such that the stereochemical consequences of its combination with I, route 3, would be observed. The dimerization of II, by way of reaction 4, unattractive on electrostatic grounds, would be expected to occur only in nonaqueous media in the presence of the stronger base, alkoxide. The three possible routes leading to pinacol reflect, in essence, the amount and strength of added base.

The observed stereochemistry may now be correlated with the above. In acid solution the dimerization of highly reactive free radicals occurs, with little preference in steric approach. That there is some preference, however, is illustrated by the data. The following conformations would be expected to result from the more fruitful attempts at bond making between approaching radicals. Structure V is formulated solely on steric grounds and, to the extent that intramolecular hydrogen bonding is not involved, would be expected on *a priori* grounds to predominate, leading one to predict that any stereoselectivity observed would favor the *meso* product. Other con-

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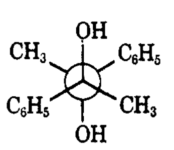
(7) Radical anions such as II have been invoked as intermediates in peroxide-induced related reactions. These were involved in steps prior to the formation of the pinacolizing radicals. For references and discussion see D. C. Neckers, *et al.*, *J. Am. Chem. Soc.*, **88**, 1265 (1966).

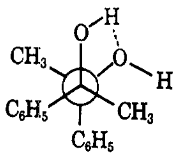
(8) S. G. Cohen and W. V. Sherman[4] have postulated the formation of the corresponding benzophenone radical ion in a similar fashion; its interaction with its parent radical was believed to lead to benzophenone and benzhydrol. No pinacol was observed.

(9) This particular radical anion has been prepared by electrolytic techniques and its esr spectrum found in accordance with predictions. Although unstable, it was estimated to have a half life of up to 60 min in dimethoxyethane: *cf.* N. Steinberger and G. K. Fraenkel, *J. Chem. Phys.*, **40**, 723 (1964).



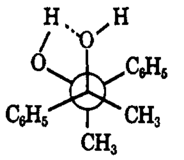
V

yields *meso*



VI

yields *dl*

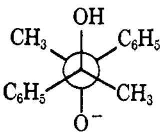


VII

yields *dl*

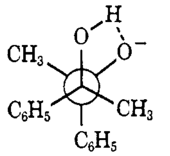
formers leading to the *meso* form require a maximum of nonbonded interactions. The fact that some preference is shown for the *dl* form strongly suggests that hydrogen bonding during the dimerization, pathway 2, is significant.

This conclusion is strengthened by an examination of the ratios observed in alkaline media. Considering runs 12, 13 and 18 as maximally reflecting pathway 3 above, we would have the corresponding conformers, VIII, IX, and X, during bond formation.



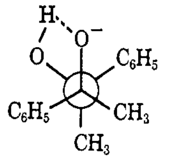
VIII

yields *meso*



IX

yields *dl*

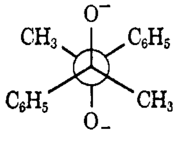


X

yields *dl*

IX and X should be appreciably more attractive relative to VIII than VI and VII were relative to V. One would therefore expect, qualitatively, a sharply increased *dl/meso* ratio as pathway 3 made a significant contribution.[10]

The remaining route to pinacol, pathway 4, should be slow and would be predicted to yield very predominantly the *meso* form, XI, based on simple polarity considerations.



XI

yields *meso*

The experimental results show a sharp initial increase in *dl/meso* ratio through 1.41 to 3.1 (average of runs 12 and 13), decreasing to approximately 2.5 over a 1000-fold increase in alkoxide concentration. This decrease probably reflects a small contribution from pathway 4.

Certain other aspects of the data in Table I for acetophenone deserve comment. Obviously any mechanism offered depends on the stability and noninterconvertibility of the diastereomeric pinacols. This has been adequately demonstrated in run 20. The difference in stability between the acetophenone pinacols and benzpinacol in alkaline media is rather striking; the successful pinacolizations reported here clearly depend on this difference.[11] Similar comments might be made about the relative thermal stabilities (contrast runs 6 and 7).[12,13]

In neutral or acidic media, the *dl/meso* ratio changes but little when cyclohexane, 2-pentanol, aqueous ethanol, or aqueous 2-propanol is substituted for 2-propanol (runs 1–10 in Table I). The trend, in general, is towards a slight increase in the *dl/meso* ratio with increasing polarity of the media. An increase of almost 100° in reaction temperature produced essentially no change in the ratio of diastereomers formed (run 6 *vs.* 7). Further, the presence of strong acid in the media (run 3), or the exclusion of proton donors (pyridine scavenger present, run 10) did not demonstrably change the *dl/meso* ratios.

The over-all yields in strongly basic media, generally in the 40–60% range, tend to decrease with increasing basicity. The reasonable assumption is that some base-dependent competitive reaction (probably of an aldol nature) is consuming the starting ketone. A rough quantitative examination by concurrent glpc and infrared spectroscopy of nonirradiated 2-propanolic solutions of acetophenone with and without potassium 2-propoxide (0.2 *N*) indicated that approximately 40% of the ketone had disappeared within the customary 18 hr reaction period in alkaline solution. This information permits the summation of a reasonable material balance and provides some measure of the relative rates of the two reactions.

The experimental results for benzaldehyde, (runs 21–29), did not prove to be satisfyingly definitive; some competitive reaction or reactions[14] precluded photopinacolization in strong base. That the difficulty is not one of pinacol stability is adequately demonstrated by run 29. The available data, however, do permit some useful comparisons. Runs 1 and 2 *vs.* 21 and 22, run 5 *vs.* 23, and run 17 *vs.* 24 and 25, all indicate a lowered stereoselectivity for benzaldehyde relative to the corresponding acetophenone runs. One might expect, *a priori*, that substituting the smaller H for CH_3 would make conformer VII more attractive relative to V, and consequently result in a higher *dl* to *meso* ratio for benzaldehyde. That the reverse is true might be attributable to two factors: the benzaldehyde radical, $C_6H_5C(OH)H\cdot$, is less stable and thus less selective than the acetophenone radical, I, and/or the methyl group of acetophenone is actually more sterically effective than the phenyl group during the dimerization step. This latter (VI) would be manifested in decreased over-all steric effects in the benzaldehyde system, causing a lower *dl* to *meso* ratio.

Several additional systems are presently under investigation and should provide additional tests of the proposed mechanism.

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[10] Some useful speculations: Pathway 2, the dimerization of ketyl radicals, may be approximated from the data as yielding the diastereomers in 1:1 ratio. If pathway 3 proceeds exclusively through IX or X (*i.e.*, yielding *dl* only), no less than 50% of the reaction would have to go by this route to yield a *dl/meso* ratio of 3:1. To the degree that VIII offers competition in this coupling process, a still higher percentage of the reaction must proceed *via* pathway 3.

[11] See comments in the first section of this paper.

[12] Benzpinacol decomposes almost quantitatively into benzophenone and benzhydrol in degassed benzene solution at 130°: D. C. Neckers and A. P. Schaap, *J. Org. Chem.*, **32**, 22 (1967).

[13] At temperatures above 100°, photochemical reduction of benzophenone produces mostly benzhydrol, apparently due to the disproportionation of the intermediate benzhydrol radicals: E. S. Huyser and D. C. Neckers, *J. Am. Chem. Soc.*, **85**, 3641 (1963).

[14] That more than one reaction is implicated is suggested by the relative rates of disappearance of benzaldehyde in alkoxide (0.2 *N*) media under conditions of irradiation *vs.* the absence of light. With irradiation, benzaldehyde completely disappears within 1 hr; in the dark, some 60% remains after 4 hr. This photochemical participation is currently under investigation.

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] $\rightarrow$ hydrobenzoin monotrichloroacetate[6] $\rightarrow$ 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.