

QUANTITATIVE STUDIES IN STEREOCHEMISTRY. XIV.  
ELECTROCHEMISTRY V.

EFFECT OF THE MEDIUM  
ON THE STEREOCHEMISTRY  
OF THE ELECTROPINACOLIZATION OF ACETOPHENONE

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Received June 23rd, 1970

The bimolecular reduction of ketones by electrochemical techniques gives rise to pinacols; unsymmetrical ketones produce the *meso* and *rac* diastereomeric products. A series of papers from this laboratory have reported and discussed the *rac/meso* ratios of diastereomers observed for acetophenone and a number of related compounds in eighty percent aqueous ethanol<sup>1</sup>. This present report describes the quite different stereochemistry observed for the title compound in aprotic media.

The pertinent results, along with selected prior data to facilitate cross-comparisons, appear in Table I.

EXPERIMENTAL

The electrolytes used were J. T. Baker analytical reagent grade and were dried over Drierite under vacuum prior to use. The dimethylformamide solvent was obtained from Matheson Scientific and contained less than 0.05% water. The acetonitrile, from J. T. Baker, contained 0.2% water.

TABLE I  
Electrochemical Bimolecular Reduction of Acetophenone

Entry	Electrode	Solvent	Electrolyte	% Pinacols	<i>rac/meso</i>
1	Hg	80% C <sub>2</sub> H <sub>5</sub> OH	LiCl	to 70	~ 1.2 <sup>a</sup>
2	Hg	80% C <sub>2</sub> H <sub>5</sub> OH	KOH	to 90	~ 2.9 <sup>b</sup>
3	Hg	dimethylformamide	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr	95	7.8
4	Hg	CH <sub>3</sub> CN	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr	96	7.2
5	Hg	CH <sub>3</sub> CN	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr	95	6.9
6	Hg	CH <sub>3</sub> CN	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr	65 <sup>c</sup>	7.0
7	Cu	CH <sub>3</sub> CN	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr	79	7.0
8	Hg	CH <sub>3</sub> CN	NaI	92	9.2
9	Hg	95% CH <sub>3</sub> CN	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr	95	5.3
10	Hg	CH <sub>3</sub> CN	(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> NBr	(99)	1.25 <sup>d</sup>

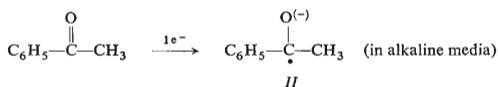
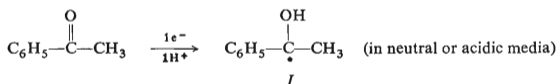
<sup>a</sup> An average of eight runs from refs<sup>2,3</sup>; <sup>b</sup> an average of nine runs from ref.<sup>2</sup>; <sup>c</sup> higher concentration study; 10 g acetophenone used, 18% unreacted; <sup>d</sup> stability study utilizing 1.0 g acetophenone plus 0.537 g of the *meso*-pinacol.

Aside from checking the specifications, no attempt was made to increase the degree of anhydrousness of the solvents.

The apparatus and the general procedure have been previously described<sup>2</sup>. Alterations in the general procedure to permit NNR analysis and a discussion of this method of evaluation have also been reported<sup>3,4</sup>. All runs, unless otherwise noted in Table I, involved one gram of acetophenone, 60 ml of solvent and a 0.25M concentration of electrolyte. All studies were carried out under conditions of constant potential ( $-1.74$  to  $-1.79$  V vs S.C.E.), with initial cell currents in the range of 100–300  $\mu$ A, for 2–7 hours.

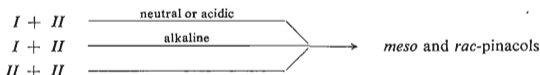
### RESULTS AND DISCUSSION

The data derived from the earlier studies in protic media were rationalized as follows:

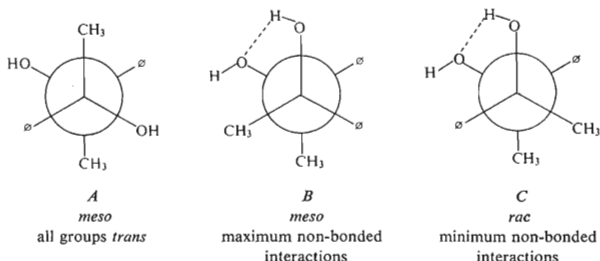


The equilibrium concentrations of *I* and *II* would reflect the amount and strength of base present.

Three possible combinations would, accordingly, have to be considered. The dimerization of *II*, involving two mutually repulsing species, would not be expected to make an appreciable contribution.

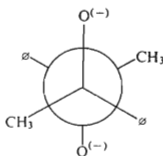


The resultant stereochemistry may be visualized as resulting from both steric and hydrogen-bonding factors. Considering the most likely conformations at the time of carbon-carbon bond formation, only *A*, leading to the *meso*-pinacol, permits no non-bonded interactions between like groups. If steric factors alone were important, predominance of the *meso* product would be predicted from this reasoning. Similarly the stabilizing effect of hydrogen bonding at the time of dimerization would lead predominantly to the *rac* form as shown in the contrast of *B* (one of two forms, each having both methyl-methyl and phenyl-phenyl non-bonded interactions) with *C* (one of two forms, each with only one such interaction). The slight preference for the *rac*-pinacol in neutral and acidic media underscores the importance of the hydrogen-bonding considerations.



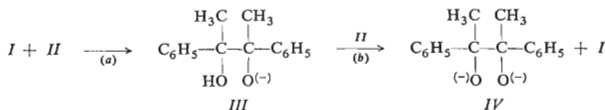
This argument is considerably strengthened from the data derived from alkaline media. Combinations of the radical *I* with the anion radical *II* should permit even stronger hydrogen bonding and greatly increase the preference for the *rac*-pinacol.

Before the aprotic media studies were undertaken, it was speculated that the results might reflect appreciable contribution from the dimerizations of the anion radical *II* which would be expected to show a strong preference for the *meso*-pinacol on both polar and steric grounds. The results, quite the opposite, an appreciably increased preference for the *rac*-pinacol, cannot



reflect such a major pathway. *rac/meso* Ratios in the range of 7–9 were found in both dimethylformamide and acetonitrile solvents, employing both sodium iodide and tetraethylammonium bromide as electrolytes. The yields were generally excellent, in excess of 90%.

The strong preference for the *rac*-form may most simply be explained as follows. Some minute fraction of the anion radical *II* formed at the electrode is protonated to form the neutral ketyl radical *I* by any of the several potential sources in the media, most likely the residual water. This combines, as discussed above, to produce predominantly the *rac*-pinacol. The likelihood



of the dimerization of *I*, appreciable in protic media, is negligibly small. The dimerization of *II* can also be neglected. The initial product of the combination of *I* and *II*, itself an alkoxy anion *III*, would normally acquire a second proton either from its surrounding media or on subsequent workup; instead, in the aprotic media, it releases its remaining proton for reuse and eventually acquires both missing protons on subsequent workup. Accordingly, a minimal supply of protons may service a very large number of anion radicals.

In support of the above, it will be noted in Table I that the formal addition of a source of protons (5% H<sub>2</sub>O) appreciably lowered (to about 5) the *rac* preference. This figure is still very considerably greater than the "neutral" media value of 1.2 in the earlier protic media studies.

To insure the results did not reflect an equilibrium situation, *i.e.* that step *a*) was truly irreversible, the reaction was carried out in the presence of preformed *meso*-pinacol (Entry 10, Table I). The preformed pinacol would be expected to yield either or both the anion *III* and dianion *IV*; if either of these collapsed to its components *I* and/or *II*, the final *rac/meso* ratio would be expected to be previously observed value of greater than 7. If it did not so collapse, the ketone present should itself go in essentially quantitative yield to pinacol in this 7 : 1 *rac/meso* ratio, which, allowing for the unchanged *meso*-pinacol, would lead to a calculated *rac/meso* value of 1.27. This figure is in excellent agreement with the observed value of 1.25.

#### REFERENCES

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#### INFLUENCE

#### OF COMPETITIVE ADSORPTION OF WATER AND FUEL ON THE ACTIVITY OF ANODES IN FUEL CELLS

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Received June 22nd, 1970

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Tungsten carbide has proved to be an acid-insoluble relatively inexpensive solid material with high activity for the anodic oxidation of hydrogen and formaldehyde in acid fuel cells<sup>1,2</sup>. On the other hand the activity for the conversion of carbon monoxide and methanol is very low<sup>2</sup>. Adsorption properties might be a reason for this different behavior. This assumption is tested by comparing the activities of tungsten carbide and Raney platinum and by investigating the adsorption of water and several simple fuels at these catalysts.