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STEREOCHEMICAL STUDIES OF THE ELECTROLYTIC REACTIONS OF ORGANIC COMPOUNDS I. ELECTROLYTIC REDUCTIONS OF AROMATIC DIKETONES

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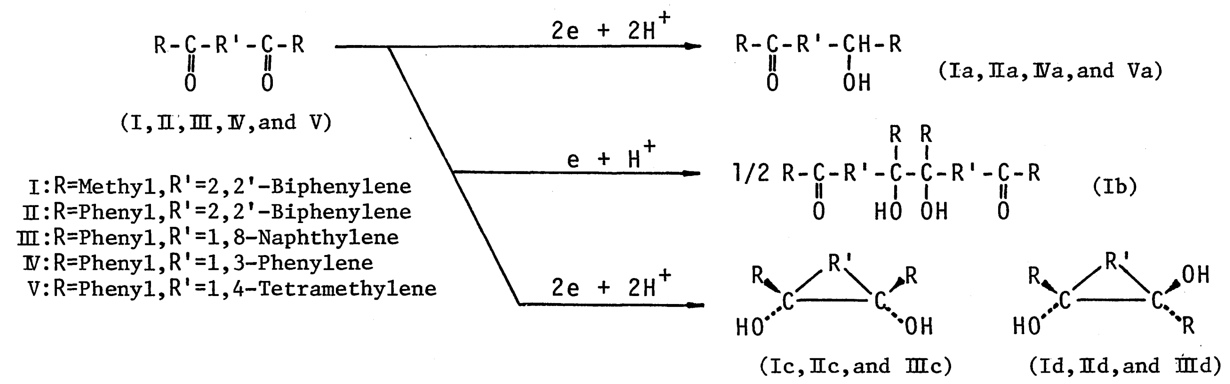
The electrolytic reductions of some aromatic diketones were carried out by means of controlled potential electrolysis in various catholytes. Reduction products were intramolecular pinacols(*cis* and *trans* *cyclic* *vicinal* diols), intermolecular pinacol, and/or hydrol. The formation ratios of the products were strongly dependent on the molecular structure of diketone, the pH of catholyte, and/or the kind of organic co-solvent.

It is well known that hydrol and pinacol are formed in the electrolysis of aromatic monoketone and the formation ratio of them depends on the pH of catholyte. On the other hand, it is probable that intramolecular pinacol, which are *cis* and *trans* *cyclic* *vicinal* diols, may be formed in the reduction of diketone in addition to hydrol and intermolecular pinacol.

In this work, five kinds of aromatic diketones, which were 2,2'-diacetylbiphenyl (I)[1], 2,2'-dibenzoylbiphenyl(II)[2], 1,8-dibenzoylnaphthalene(III)[3], 1,3-dibenzoylbenzene(IV)[4], and 1,4-dibenzoylbutane(V)[5], were electrolyzed at a mercury cathode in aqueous organic solvents. An electrolytic cell was the same as described in a previous work.[6] A mercury pool(area, 12 cm^2) was used as a cathode, while the anode was a platinum disc(diameter, 2 cm). The catholyte and anolyte were 60 ml of organic solvent containing water in a concentration of 20 vol %. Supporting electrolytes were used in a concentration of 5 wt %. One gram of diketone was added in the catholyte and was completely dissolved. Electrolysis was carried out at a constant cathodic potential, at which an initial cathodic current density was 22 amp/cm^2 and no hydrogen evolution was observed. When a cathodic current density lowered to 1 amp/cm^2, electricity was turned off. Electrolysis was run at about



I:R=Methyl,R'=2,2'-Biphenylene
II:R=Phenyl,R'=2,2'-Biphenylene
III:R=Phenyl,R'=1,8-Naphthylene
IV:R=Phenyl,R'=1,3-Phenylene
V:R=Phenyl,R'=1,4-Tetramethylene

Table 1 . The Properties of Products

Product	Formula	Recrystallization solvent	Mp (Literature) °C	IR spectrum cm^{-1}		Mass spectrum M^+	Elemental analysis, %			
							Found		Calcd.	
				$\nu_{C=O}$	ν_{O-H}		C	H	C	H
Ia	$C_{16}H_{16}O_2$	aq. Acetic acid	130-132	1680	3400	240	79.75	6.62	79.97	6.71
Ib	$C_{32}H_{30}O_4$	aq. Methanol	155	1660	3450	478^a, 460^b	79.55	6.19	80.31	6.32
Ic,d	$C_{16}H_{16}O_2$	Chloroform	161-162^{c,d} (164)$^{1)}$	-	3400	240	79.25	6.76	79.97	6.71
IIa	$C_{26}H_{20}O_2$	Ethanol	180-182	1660	3470	364	85.14	5.41	85.69	5.53
IIc	$C_{26}H_{20}O_2$	Ligroin	200-201^d (201-201.5)$^{8)}$	-	3460	364	85.40	5.69	85.69	5.53
IId	$C_{26}H_{20}O_2$	Ethanol	179-180^d (178-179)$^{2)}$	-	3480	364	85.22	5.50	85.69	5.53
IIIc	$C_{24}H_{18}O_2$	Acetic acid	174-175^d (176-177)$^{8)}$	-	3220	338	84.70	5.21	85.18	5.36
IIId	$C_{24}H_{18}O_2$	Ethanol	155-156^d (154)$^{3)}$	-	3360	338	85.20	5.19	85.18	5.36
IVa	$C_{20}H_{16}O_2$	aq. Ethanol	126-128	1635	3450	288	83.69	5.39	83.31	5.59
Va	$C_{18}H_{20}O_2$	Methanol	98-100	1670	3450	268	80.13	7.59	80.56	7.51

a:Very weak. b:Strong. c:The value of a sample recrystallized five times. The original sample, of which the melting point was lower, was probably a mixture of cis and trans isomers. d:A mixed melting point with the authentic sample showed no depression.

Table 2 . The Conditions and Results of Electrolytic Reductions of Diketones

Diketone	Supporting electrolyte	Organic co-solvent	Cathode potential (V vs.SCE)	Yield of product,%			Passed electricity (Fr/mole)
				Intramolecular pinacol(cis/trans)	Intermolecular pinacol	Hydrol	
I	H_2SO_4	Methanol	-0.98	61(-)	-	12	2.0
I	AcONa-AcOH	Methanol	-1.25	34(-)	-	29	2.0
I	AcONa	Methanol	-1.40	19(-)	45	-	1.6
I	NaOH	Methanol	-1.45	-	93	-	1.0
II	H_2SO_4	THF	-0.90	28(10)	-	41	2.0
II	H_2SO_4	DMF	-0.93	61(3)	-	7	2.0
II	NaOH	THF	-1.50	8(11)	-	62	2.0
II	NaOH	DMF	-1.50	52(3)	-	16	2.0
III	H_2SO_4	THF	-0.75	87(∞)	-	-	2.0
III	H_2SO_4	DMF	-1.00	72(5)	-	-	1.8
III	NaOH	THF	-1.50	84(0)	-	-	2.1
III	NaOH	DMF	-1.70	87(0)	-	-	1.9
IV	H_2SO_4	THF	-0.77	-	-	90	1.9
V	H_2SO_4	THF	-0.92	-	-	94	2.0

10 °C. After electrolysis, the catholyte was diluted with 500 ml of water, was neutralized with acid or alkali, and then was stored overnight in a refrigerator. The resulting precipitate was filtered and each product was isolated by repeated fractional recrystallization from organic solvents. Purified products were confirmed by melting points, elementary analyses, and IR and mass spectra shown in Table 1, and also by coulometric electron-numbers(passed electricity) shown in Table 2. No unreacted diketone was recovered in all electrolyses.

Electrolysis results are summarized in Table 1.

Electrolytic Reduction of 2,2'-Diacetylbiphenyl(I) As shown in the table, the results of electrolyses of I varied with the pH of catholyte. In acidic media, intramolecular pinacol(Ic and/or Id) and hydrol(Ia) were reduction products. In a weakly alkaline medium, intermolecular pinacol(Ib) was formed in addition to intramolecular pinacol, but no Ia was obtained. On the other hand, Ib was a sole product in a strongly alkaline medium. The amount of passed electricity per one mole of diketone was considerably correlative with the distribution of products in each electrolysis. The steric structures of Ib, Ic, and Id could not be determined.

Electrolytic Reduction of 2,2'-Dibenzoylbiphenyl(II) Electrolyses of II were carried out in strongly acidic and alkaline solutions containing THF or DMF as a co-solvent. Reduction products were two isomeric intramolecular pinacols(IIc: cis and IId: trans forms) and hydrol(IIa) , and no intermolecular pinacol was obtained. No formation of intermolecular pinacol is seemed to be due to steric hindrance. In the electrolysis of II , solvent effect was very predominant, while the effect of pH was minor. Namely, in the catholytes containing THF IIa was major product and the cis/trans ratios of intramolecular pinacol were larger than those in DMF solutions. All the tendencies were reverse in DMF. It is also interesting to note that the electrolytic reductions resulted more than one of the cis/trans ratios, contrary to anticipation from the thermodynamical stabilities of both isomers,7) as well as reductions with chemical reducing reagents such as PhMgI,8) Mg-MgI$_2$,10) Zn-KOH,2, 10) Zn-AcOH,10) and sodium amalgam.10)

Electrolytic Reduction of 1,8-Dibenzoylnaphthalene(III) Reduction products of III were cis(IIIc) and trans(IIId) intramolecular pinacols, while neither intermolecular pinacol nor hydrol was formed. No formation of intermolecular pinacol is seemed to be due to rapid intramolecular cyclization owing to the closely fixed configuration of the two carbonyl groups of III. It is also noticable that the electrolytic reduction of III in strongly alkaline media afforded only trans isomer, while the reductions with chemical reducing reagents such as Mg-MgI$_2$,11) sodium amalgam,12) and PhMgI8) afforded only *cis* isomer. Contrary to the case of II , pH effect was more predominant than solvent effect.

Electrolytic Reductions of 1,3-Dibenzoylbenzene(IV) and 1,4-Dibenzoylbutane(V) Either IV or V gave only hydrol(IVa or Va) in acidic medium. No formation of intramolecular pinacol in the reductions of IV and V is seemed to be due to the generation of high structual strain in cylcization and to the long distance between two carbonyl groups respectively. On the other hand, the reductions in an alkaline medium afforded amorphous substances which could not be identified.

Discussion on Mechanism from Stereochemical Aspect A number of studies on the stereochemistry of pinacols produced by electrolytic reductions of aromatic monoketones and monoaldehydes have been performed. For instance, Stocker et al.13) found that *dl*/*meso* ratio in the mixture of pinacols derived from acetophenone ranges from 1.0 to 1.4 in acidic media and from 2.5 to 3.2 in alkaline media, under a wide variety of electrolytic conditions. It is an established theory that pinacol is formed by coupling of radicals such as $>\dot{C}$-OH, $>\dot{C}$-O$^-$, and $>\dot{C}$-O$^-$M$^+$.14) The excess formation of *dl* pinacol was rationalized as due to favorable inter-radical hydrogen bonding in the transition state for the formation of *dl* isomer. This postulate was also supported by the fact that the electrolytic reduction of 2-acetylpyridine afforded *meso* pinacol anticipated on a simple steric ground exclusively, presumably, because of strong intramolecular hydrogen bonding of a hydroxy group with a nitrogen atom in a radical intermediate.

On the other hand, there have been few papers dealing with the stereochemistry of *cyclic vicinal* diol(intramolecular pinacol) produced by the electrolytic reduction of diketone.16,17) In the view of thermodynamical stability, *cis* and *trans* cyclic diols are corresponding to *meso* and *dl* pinacols respectively. However, such a correspondence may reverse in the case where the steric structure of *cyclic* diol or pinacol is controlled by the inter-radical hydrogen bonding in the transition state.

Gourley et al. found that the *cis*/*trans* ratios of diols produced by electrolytic reduction of 1,5-di-(4-methoxyphenyl)- and 1,5-di-(4-hydroxyphenyl)-pentane-dions in an alkaline medium were 21.6 and 0.9 respectively.16) These facts were rationalized as due to favorable inter-radical hydrogen bonding in the case of the former and to strong electrostatic repulsion, which cancels the effect of the hydrogen bonding, between two negatively charged aromatic rings in the case of the latter. They also obtained diols in the *cis*/*trans* ratios such as 1.5 and 2.3 from 2,2'-di-(4-methoxybenzoyl)- and 2,2'-di-(4-hydroxybenzoyl)-biphenyls which are analogous compouds to II. However, these facts could not be rationalized by the above theory. There is also a similar problem to this in the reductive coupling of monoketone having a hydroxy group.18)

To avoid such complications, diketones having no substituent were introduced in this work. It is the most interesting result that the cis/trans ratios of diols from II and III depended almost exclusively on the kind of organic co-solvent and on the pH of catholyte respectively.

Since the two benzoyl groups of II are as far apart as possible in an adsorption state on cathode surface because of steric hindrance, rotation around a phenyl-phenyl bond should be involved in the course of the formation of intramolecular pinacol by cyclization of a biradical intermediate. Such a rotation may obliged the cyclization to occur in such an apart region from a cathode surface that solvent effect may appear. Though no enough strict theory to explain the difference between result in THF and that in DMF could not be established, it might be argued at least that the solvation of organic solvent to intermediate disturbs hydrogen bonding in the transition state and forces the cis/trans ratio to decrease. If the solvation of DMF is stronger than that of THF,19) the above argument may be actualized.

Since III has a rigid structure and its two carbonyl groups are so close to each other that the cyclization of biradical can occur on the surface or in the immediate neighborhood of a cathode, no solvent effect may appear. The predominant formation of cis isomer in acidic media is rationalized as due to strong hydrogen bonding, which is not disturbed by solvation, in the transition state where a neutral biradical derived from protonated diketone cyclizes. On the other hand, since neither hydrogen bonding nor solvation contributes in alkaline media, a thermodynamically advantageous trans isomer is formed exclusively.7)

Although Gourley et al.16) had obtained considerable amounts of the corresponding non-cyclic diols in the electrolyses of some analogous diketones to II and III in alkaline media, no diol could be obtained in this work. This difference may be caused by more positive cathode potentials(-1.5 to -1.7 V vs. SCE) in this work than that(-2.0 V) in the case of Gourley et al. The effects of cathode potential and pH will be further discussed in connection with the polarographic behaviors of diketones in the next paper.21)

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