Stereochemical Studies of the Electrolytic Reactions of Organic Compounds. V.† The Electro-reductive Cyclization of 1-Acyl-8-benzoylnaphthalenes to 1,2-Acenaphthenediols

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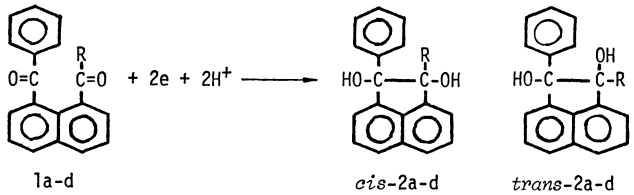
The electrolytic reductions of several 1-acyl-8-benzoylnaphthalenes were carried out by means of controlled potential electrolysis at a mercury cathode in various catholytes. The isomeric ratio of the *cis*- and *trans*-1,2-acenaphthenediols thus formed depended on the kind of acyl group, supporting electrolyte, organic solvent in the catholyte, and cathode potential applied. The mechanism of the reductive cyclization is discussed from the stereochemical point of view, and it is proposed that the cyclization may occur not only by the intramolecular coupling of the biradical intermediate, but also by the intramolecular nucleophilic addition of the anionic part of the carbanion intermediate to its unreacted carbonyl group.

A number of studies of the stereochemistry of *vic*-diols produced by the electro-reductive dimerization of aromatic ketones and aldehydes have been performed. For instance, Stocker and Jenevein[1,2] found that the *dl*/*meso* ratio of the diol derived from acetophenone ranged from 1.0 to 1.4 in acidic media and from 2.5 to 3.2 in alkaline media, under a wide variety of electolytic conditions. These facts were explained as resulting from hydrogen bonding between radical intermediates in the transition state favorable for the formation of the *dl* isomer.

On the other hand, there have been a few papers[3–5] dealing with the stereochemistry of cyclic *vic*-diols produced by the electro-reductive cyclization of diketones. Gourley and Grimshaw[3] reported that the *cis*/*trans* ratios of the cyclic *vic*-diols produced by the reductive cyclization of 1,5-bis(4-methoxybenzoyl)-pentane and 1,5-bis(4-hydroxybenzoyl)pentane in an alkaline medium were 21.6 and 0.9 respectively. These facts were explained as resulting from hydrogen bonding favorable for the formation of the *cis* isomer in the case of the former, and to the strong electrostatic repulsion between the two negatively charged aromatic rings in the case of the latter. They also obtained cyclic *vic*-diols in such *cis*/*trans* ratios as 1.5 and 2.3 from 2,2′-bis(4-methoxybenzoyl)biphenyl and 2,2′-bis(4-hydroxybenzoyl)biphenyl respectively. However, these facts contradict the above theory. There is also an ambiguous point in the reductive dimerization of hydroxy ketones.[1,6]

In a previous work,[5] several aromatic diketones were electrolytically reduced under a variety of conditions, and it was found that the distribution of the products, which were cyclic and non-cyclic *vic*-diols and secondary alcohols, depended on the molecular structure of the diketones and on the electrolytic conditions. Of the diketones used, 1,8-dibenzoylnaphthalene (**1a**) gave only the corresponding cyclic *vic*-diol (1,2-acenaphthenediol, **2a**).

In this work, in addition to **1a**, three kinds of 1-acyl-8-benzoylnaphthalenes (**1b**—**d**) were subjected to electrolysis in order to clarify the mechanism of the reductive cyclization from the stereochemical point of view. The diacylnaphthelenes, **1b**—**d**, are characterized by their unsymmetrical molecular structures.



1a-d *cis*-2a-d *trans*-2a-d

a: R=C_6H_5
b: R=4-CH_3O-C_6H_4
c: R=4-HO-C_6H_4
d: R=CH_3

Results and Discussion

Synthesis of 1-Acyl-8-benzoylnaphthalenes (1a—d). 1,8-Dibenzoylnaphthalene (**1a**) was prepared according to the method of Beschke.[7] The routes of synthesizing the unsymmetrical diacylnaphthalenes (**1b**—**d**) were newly designed for this work.

At the first stage of the synthesis, 2-phenyl-2-hydroxy-1-acenaphthenone (**3**), which is an intermediate common to **1b**—**d**, was prepared from equimolar acenaphthenequinone and phenylmagnesium bromide in a 94% yield. The structure of the new compound, **3**, was determined by elemental analysis and by a study of the IR and mass spectra. At the second stage, **3** was converted into *trans*-1-phenyl-2-(4-methoxyphenyl)-1,2-acenaphthenediol (**2b**) and *trans*-rich 1-phenyl-2-methyl-1,2-acenaphthenediol (**2d**) by means of a Grignard reaction with 4-methoxyphenylmagnesium bromide and methylmagnesium iodide respectively. Finally, **2b** and **2d** were oxidized with chromium(VI) oxide to give 1-(4-methoxybenzoyl)-8-benzoylnaphthalene (**1b**) and 1-acetyl-8-benzoylnaphthalene (**1d**) respectively. 1-(4-Hydroxybenzoyl)-8-benzoylnaphthalene (**1c**) was prepared by the treatment of **1b** with boron tribromide.[8] The structures of the new compounds, **1b**—**d**, were established by elemental analysis and by a study of the IR and mass spectra.

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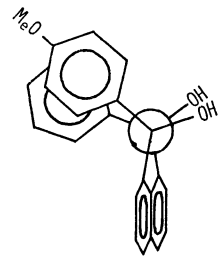
Determination of the Configuration of 1,2-Acenaphthenediol (2a—d). Since both *cis*-**2a**[7] and *trans*-**2a**[9] are known compounds, the measurement of their melting points served as the method of identification.

The diols, **2b—d**, are unknown compounds. The **2b** diol synthesized by the Grignard reaction differed from that synthesized by the magnesium reduction[10] of **1b** in its melting points, in the chemical shift of the methyl protons in the NMR spectra, and in the IR absorption bands of hydroxyl groups. Generally, the *cis* isomers of cyclic *vic*-diols, such as 1,2-acenaphthenediols and 9,10-dihydro-9,10-phenanthrenediols, showed higher melting points than the *trans* isomers.[9,10] Since the conformation of the phenyl and 4-methoxyphenyl groups of *cis*-**2b** shown in Scheme 1 seems to be more plausible than any other conformations in view of the steric requirement, the methyl protons of *cis*-**2b** are probably magnetically shielded by the phenyl group; consequently, a signal for the methyl protons would appear at a higher magnetic field in the NMR spectrum. From these considerations, the **2b** synthesized by the magnesium reduction, which melted at a higher temperature and which showed the NMR signal for methyl protons at a higher magnetic field than *trans*-**2b**, was considered to be the *cis* isomer. Both isomers also differed from one another in the IR spectrum in the OH-stretching band region. The *cis* isomer showed a broad band at about 3300 cm^{-1}. Such a low frequency seems to be the result of intramolecular hydrogen bonding. On the other hand, the *trans* isomer showed two sharper bands at 3550 and 3380 cm^{-1}. The higher-frequency band may be assigned to free hydroxyl groups, while the lower-frequency band may be the result of intermolecular hydrogen bonding.[12]



Scheme 1. Favorable conformation of *cis*-**2b**.

The *cis* and *trans* isomers of **2d** were separated by the fractional recrystallization of an isomeric mixture prepared by the Grignard reaction. The stereochemistry of the isomers was determined, similarly to the case of

Table 1. Electrolytic reduction of 1-acyl-8-benzoylnaphthalenes to 1,2-acenaphthenediols

Compound	Supporting electrolyte	Organic co-solvent	Cathode potential V *vs.* SCE	Quantity of electricity passed $\times 10^5$ C/mol	1,2-Acenaphthenediol Yield (%)	1,2-Acenaphthenediol *cis*: *trans* (%)
1a	H_2SO_4	THF	−0.75	1.9	87[a]	100: 0
1a	H_2SO_4	DMF	−1.00	1.7	72[a]	85: 15
1b	H_2SO_4	THF	−0.67	2.1	100	80: 20
1b	H_2SO_4	THF	−0.76	2.0	95	69: 31
1b	H_2SO_4	DMF	−1.16	2.1	100	70: 30
1b	H_2SO_4	DMF	−1.38	2.7	100[b]	59: 41
1c	H_2SO_4	THF	−0.74	2.7	70[c]	57: 43
1c	H_2SO_4	THF	−0.89	2.0	75[c]	50: 50
1c	H_2SO_4	THF	−1.13	1.7	78[c,d]	50: 50
1c	H_2SO_4	DMF	−0.88	2.5	70[c]	55: 45
1c	H_2SO_4	DMF	−0.97	1.6	75[c,d]	49: 51
1c	H_2SO_4	DMF	−1.10	2.5	92[c]	49: 51
1a	NaOH	THF	−1.50	2.0	84	0: 100
1a	NaOH	DMF	−1.70	1.8	87	0: 100
1b	NaOH	THF	−1.40	2.3	100	0: 100
1b	NaOH	THF	−1.50	2.7	100	0: 100
1c	NaOH	THF	−1.35	1.5	53[d]	9: 91
1c	NaOH	THF	−1.55	2.4	67[d]	12: 88
1c	NaOH	—	−1.30	1.5	—[d,e]	11: 89
1c	NaOH	—	−1.47	1.5	—[d,e]	19: 81
1a	AcONa	AcOH	−1.50	2.4	78[b]	59: 41
1b	AcONa	AcOH	−1.50	3.4	50[b,d]	66: 34
1b	AcONa	AcOH	−1.60	5.8	50[b,d]	62: 38
1c	AcONa	AcOH	−1.46	1.8	50[b,d]	77: 23
1c	AcONa	AcOH	−1.56	1.8	50[b,d]	73: 27
1d	AcONa	AcOH	−1.30	1.7	78[d]	95: 5
1d	AcONa	AcOH	−1.50	2.9	80[b,d]	85: 15

a) Yield after purification. b) A vigorous hydrogen evolution was observed. c) A part of the 1,2-acenaphthenediol formed underwent acid-catalyzed pinacol rearrangement during electrolysis. d) A considerable amount of the unreacted naphthalene was recovered. e) The yield was not estimated.

2b, from considerations of their melting points and by a study of their IR and NMR spectra.

Determination of the Isomeric Formation Ratio of 1,2-Acenaphthenediols (2a—d). The isomeric ratio of **2a** formed in electrolysis was determined by fractional precipitation. The isomeric ratios of **2b** and **2d** were determined from the intensity of NMR signals for their methyl protons. Because the direct determination of the isomeric ratio of **2c** was difficult, the determination was carried out after **2c** was converted into **2b** with methyl sulfate. It was confirmed by a repetition of a methylation-demethylation cycle that no isomerization occurred during the methylation.

Electrolytic Results. The electrolytic conditions and results are summarized in Table 1. The *cis*/*trans* ratio of the 1,2-acenaphthenediols formed depended on the substituent of the starting naphthalenes, the cathode potential applied, the supporting electrolyte, and the organic co-solvent added to the catholyte to dissolve the naphthalenes. No by-products, such as 1-acyl-8-(hydroxymethyl)naphthalenes or 1,8-di(hydroxymethyl)naphthalenes, could be separated by column chromatography.

As is shown in Table 1, **1a** and **1b** gave the *cis*-rich diols in strongly acidic media, while **1c** gave the *cis* and *trans* diols in almost equal quantities. A part of the diol from **1c** was rearranged by sulfuric acid into the corresponding pinacolone during electrolysis. Since the pinacol rearrangement of *cis*- and *trans*-1,2-acenaphthenediols proceeds at almost the same rate in a medium containing water,[11] the *cis*/*trans* ratio measured after electrolysis probably corresponds to the real formation ratio of the isomers.

The formation of the thermodynamically stable *trans* isomer was predominant in strongly alkaline media.

In an weakly acidic solution, **1a—d** gave the *cis*-rich diols. The naphthalene, **1d**, which was condensed by water elimination into 3-phenyl-1-phenalenone in strongly acidic and alkaline media, could be electrolyzed only in this solution.

Polarography. The naphthalenes, **1a—d**, mostly showed very complicated multiple reduction waves in their polarograms. The half-wave potentials for the first waves only, therefore, can be estimated from the polarograms.

Table 2. Half-wave potentials of the polarographic first waves of 1-acyl-8-benzoylnaphthalene[a]

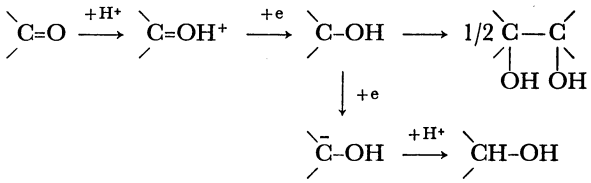
Compound	Supporting electrolyte	Organic co-solvent	$E_{1/2}$ V *vs.* SCE
1a	H_2SO_4	DMF	−0.58
1b	H_2SO_4	THF	−0.56
1b	H_2SO_4	DMF	−0.63
1c	H_2SO_4	THF	−0.54
1c	H_2SO_4	DMF	−0.63
1a	AcONa	AcOH	−0.90
1b	AcONa	AcOH	−0.87
1c	AcONa	AcOH	−0.89
1d	AcONa	AcOH	−0.88
1a	NaOH	DMF	−1.23
1b	NaOH	THF	−1.26
1c	NaOH	—	−1.27

a) Measured in *ca.* 5×10^{-4} M of the concentration of the naphthalene in an electrolytic solution similar to one used for the macro electrolysis.

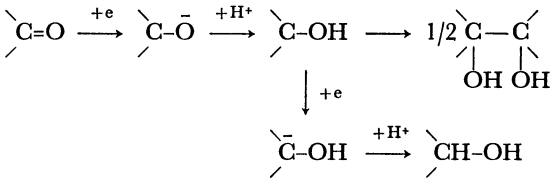
The reduction potential of an aromatic carbonyl compound generally depends on the substituents on its aromatic ring, and the dependence follows Hammet's rule.[13] For example, the polarographic half-wave potentials of 4-methoxy- and 4-hydroxybenzophenones are more negative by 100 and 170 mV respectively than that of unsubstituted benzophenone in an acidic medium. The half-wave potentials of **1a—d** were close to each other under the same conditions, as is shown in Table 2. This fact may suggest that the first one-electron transfer occurs at an unsubstituted benzoyl group in all of the naphthalenes.

Discussion of the Mechanism of the Reductive Cyclization from Stereochemical Aspects. The general reduction mechanism of carbonyl compounds was shown by Zuman[14,15] as follows:[16]

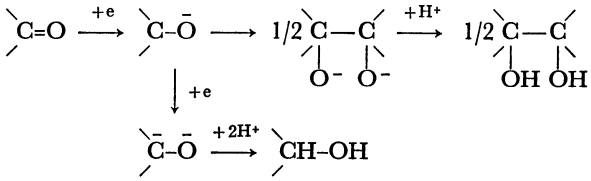
In acidic media;



in the medium pH-range;



and in alkaline media;

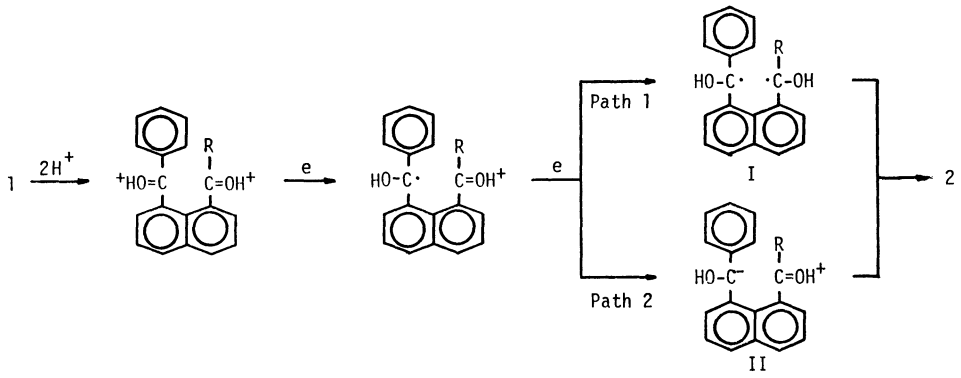


In the reduction of diketones, the second electron-transfer may occur not only at a radical carbon, but also at an unreacted carbonyl carbon. This problem could not be solved polarographically, because the naphthalenes, **1a—d**, showed multiple reduction waves which were ill-defined except for the first waves.

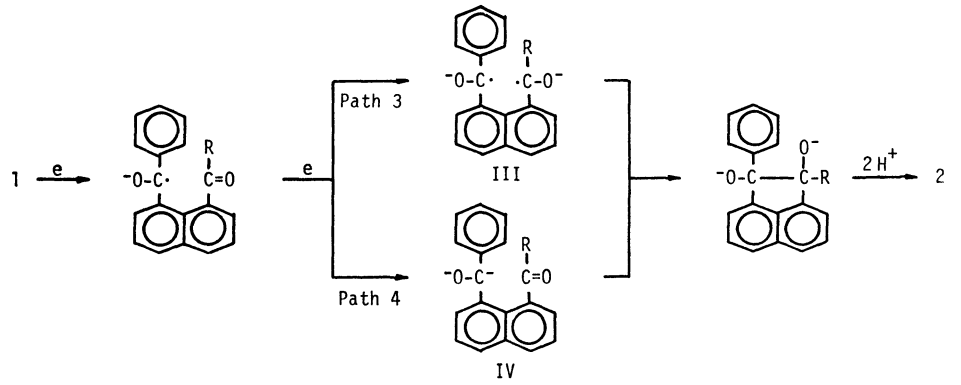
In Schemes 2, 3, and 4, two types of mechanisms for the cyclization are presented. One is based on the coupling of a biradical, and the other, on the nucleophilic addition of the carbanion.

Intramolecular hydrogen bonding in the intermediates would cause the formation of the *cis* isomer. The strength of the hydrogen bonding of a hydroxyl group with an other group containing an oxygen atom would increase in this order: $^+$HO=C, HO–C, O=C, and $^-$O–C, in view of the electron density on the oxygen atom.

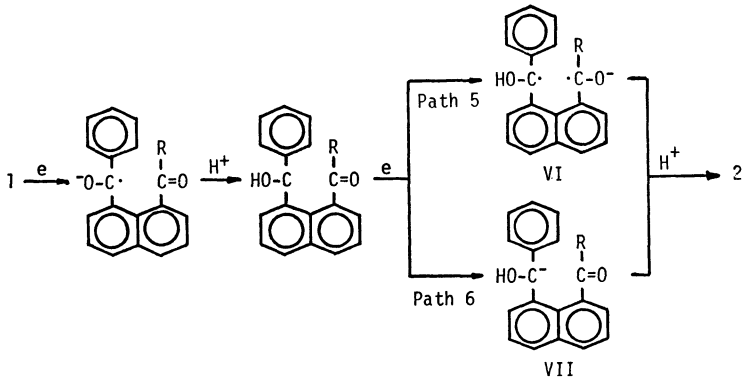
As is shown in Table 1, in a strongly acidic medium a marked substituent effect on the isomeric ratio was



Scheme 2. Possible mechanisms in strongly acidic solutions.



Scheme 3. Possible mechanisms in alkaline solutions



Scheme 4. Possible mechanisms in an weakyl acidic solution.

observed. An electron-releasing substituent on a substituted benzoyl group (R) would weaken the intramolecular hydrogen bonding in a carbanion intermediate (II) in Path 2 by promoting the protonation of the carbonyl group to decrease the ratio of the *cis* isomer, while such a substituent effect can not be expected in a biradical intermediate (I). The promotion of the protonation is essentially due to an increase in the basicity of the carbonyl group. The substituent effect observed suggests that Path 2 may be included in the cyclization process, but there is no experimental evidence for excluding Path 1. The influence of the cathode potential on the isomeric ratio may be explained as resulting from different potentials for the second electron-transfer in Paths 1 and 2, if the potential for the former is somewhat more positive than that for the latter. Whether the solvent effect is completely independent of the cathode potential is questionable.

In strongly alkaline media (see Scheme 3), where Paths 3 and 4 are possible, the *trans* isomers were predominantly formed. Since there is no contribution of hydrogen bonding in the cyclization process in either path, such electrolytic results seem reasonable. Path 3 may result in the formation of a larger amount of the *trans* isomer by the contribution of electrostatic repulsion between two negatively charged oxygen atoms than in Path 4. The exclusive formation of the *trans* isomers in the cases of **1a** and **1b** can be explained by Path 3.

Also, the formation of a small amount of the *cis* isomer in the case of **1c** may be explained as resulting from

another electrostatic repulsion, which would not be strong, between a phenolate anion (p-C_6H_4–O^-) and an oxygen anion at the opposite side of an intermediate (III) in Path 3. However, the influence of the cathode potential on the isomeric ratio can not be explained by Path 3. It seems that the reduction potential of a carbonyl group is more positive than that of the corresponding anion radical (Ċ–O^-) formed by one-electron transfer.[14,15] As the reduction potential of the carbonyl group shifts negatively when its basicity is increased by electron-releasing substituents,[13] the potential for the second electron-transfer in Path 3 may be very close to that in Path 4 in the case of **1c**, the substituent (p-C_6H_4–O^-) of which is a very strong electron-releasing group. The increase of the *cis* isomer in electrolysis at a more negative potential may be explained as resulting from the increase in the contribution of Path 4, which is competitive with Path 3, since in Path 4 the electrostatic repulsion should be weaker.

In acetic acid–sodium acetate, the manner of the substituent effect was similar to that in the alkaline media. Since the protonation of the carbonyl group would be very slight in this solution,†† the reduction mechanisms shown in Scheme 4 may be possible.[14] If the influence of the cathode potential on the isomeric ratio can be neglected compared with that of the substituent, Path 6 may be more favorable than Path 5 as an explanation of the electrolytic results. The predominant formation of the *cis* isomer in the case of **1d** may be the result of the overlapping of the strong electron-releasing and weak steric hindrance effects of the methyl group.

In summary it can be concluded from the above discussion that the nucleophilic addition process (Paths 2, 4, and 6) should be included in the reductive cyclization of 1,8-diacylnaphthalenes, without excluding the radical coupling process (Paths 1, 3, and 5); *i.e.*, the two processes are in competition with each other.

Experimental

*Synthesis of 1-Acyl-8-benzolylnaphthalenes (**1a—d**). 1,8-Dibenzoylnaphthalene (**1a**)*: *trans*-1,2-Diphenyl-1,2-acenaphthenediol (*trans*-**2a**) was prepared from one mole of acenaphthenequinone and two moles of phenylmagnesium bromide, and was then recrystallized from ethanol. Yield, 85%; mp 155—156 °C (lit,[7] 155—156 °C), and ν_{O-H} 3360 and 3420 cm^{-1}. The 1,2-acenaphthenediol obtained was oxidized with chromium (VI) oxide in acetic acid to give **1a** in a 30% yield. The crude product was recrystallized from a mixture of acetone and ethanol. Mp 187—190 °C (lit,[7] 190 °C), $\nu_{C=O}$ 1620 cm^{-1}, and *m/e* 336 (M^+). Found: C, 85.55; H, 4.56%. Calcd for $C_{24}H_{16}O_2$: C, 85.69; H, 4.79%.

*1-(4-Methoxybenzoyl)-8-benzoylnaphthalene (**1b**)*: A phenylmagnesium bromide solution, which has been prepared from 8.0 g of magnesium, 52.8 g of bromobenzene and 250 ml of THF, was added drop by drop, to 50 g of acenaphthenequinone suspended in 1500 ml of THF at room temperature. After stirring for 5 h, 50 ml of a saturated ammonium chloride solution was added to the reaction mixture, and then the resulting precipitates were filtered off. The filtrate was evaporated under reduced pressure. The residual red oil was extracted with 200 ml of benzene, and the benzene extract was washed with 500 ml of 5% sulfuric acid. The benzene solution was dried over anhydrous sodium sulfate and then evaporated to dryness under reduced pressure. The recrystallization of the residual solid from 2-propanol afforded 67 g (Yield 94%) of 2-phenyl-2-hydroxyl-1-acenaphthenone (**3**) as yellow plates. Mp 146—147 °C, $\nu_{C=O}$ 1710 cm^{-1}, ν_{O-H} 3500 cm^{-1}, and *m/e* 260 (M^+). Found: C, 83.31; H, 4.75%. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65%.

A 4-methoxyphenylmagnesium bromide solution, which had been prepared from 5.6 g of magnesium, 43.2 g of 4-methoxybromobenzene, and 200 ml of THF, was added to 20.0 g of **3** dissolved in 100 ml of THF. After stirring for 2 h, 20 ml of a saturated ammonium chloride solution was added to the reaction mixture, and then the resulting precipitates were removed by filtration. When the filtrate was evaporated, an oily substance remained. The oil was solidified by treatment with a small amount of methanol. The recrystallization of the solid from 2-propanol afforded 22.1 g (yield, 83%) of *trans*-1-phenyl-2-(4-methoxyphenyl)-1,2-acenaphthenediol (*trans*-**2b**)††† as white needles. Mp 111—112 °C, *m/e* 368 (M^+), ν_{O-H} 3380 and 3550 cm^{-1}, and δ for methyl protons 3.81 ppm. Found: C, 81.21; H, 5.23%. Calcd for $C_{25}H_{20}O_3$: C, 81.50; H, 5.47%.

Into 20.0 g of *trans*-**2b** dissolved in 100 ml of acetic acid we added drop by drop, 36.7 g of a 10% aqueous chromium(VI) oxide solution. After having been allowed to stand for 1.5 h, the reaction mixture was poured into cold water, and the resulting aqueous solution was repeatedly extracted with ether. The ethereal extract was washed with a saturated sodium carbonate solution and then with water. The ethereal solution was dried over anhydrous sodium sulfate and then evaporated. The resulting tar was solidified by treatment with a mixture of ethyl acetate and petroleum ether. The recrystallization of the solid from ethanol afforded 13.6 g (yield, 68%) of 1-(4-methoxybenzoyl)-8-benzoylnaphthalene (**1b**) as white needles. Mp 111—112 °C, $\nu_{C=O}$ 1650 and 1630 cm^{-1}, *m/e* 366 (M^+), and δ for methyl protons 3.86 ppm. Found: C, 81.96; H, 4.71%. Calcd for $C_{25}H_{18}O_3$: C, 81.95; H, 4.95%.

*1-(4-Hydroxybenzoyl)-8-benzoylnaphthalene (**1c**)*: In 500 ml of dichloromethane, 10.0 g of *trans*-**1b** was reacted with 20.0 g of boron tribromide at room temperature for 4 h. The reaction mixture was then poured into 500 ml of 5% sodium hydroxide. When the aqueous layer was neutralized with aqueous sulfuric acid, white solides were precipitated. Recrystallization from benzene afforded 8.0 g (yield, 80%) of **1c** as white needles. Mp 115 °C (dec), $\nu_{C=O}$ 1650 and 1630 cm^{-1}, ν_{O-H} 3260 cm^{-1}, and *m/e* 352 (M^+). Found: C, 81.74; H, 4.09%. Calcd for $C_{24}H_{16}O_3$: C, 81.80; H, 4.58%.

*1-Acetyl-8-benzoylnaphthalene (**1d**)*: A methylmagnesium iodide solution, which has been prepared from 4.2 g of magnesium, 25.0 g of methyl iodide, and 200 ml of ether, was added to 15.0 g of **3** dissolved in 50 ml of THF. The reaction mixture was refluxed for 3 h, and then a 100-ml portion of a saturated ammonium chloride solution was added. The organic layer was dried over anhydrous sodium sulfate and then evaporated. The residual red oil was solidified by treatment with a small amount of methanol. The recrystallization of the solid from a

†† It has been suggested, on the basis of the UV spectroscopic data, that a carbonyl compound is in protonation equilibrium in strongly acidic solutions.[17]

††† The *cis* isomer (*cis*-**2b**) was also prepared by the iodine-catalyzed magnesium reduction of **1b** in benzene at 80 °C. Yield, 100%; mp 177—178 °C, *m/e* 368 (M^+), and ν_{O-H} 3300 cm^{-1}, and δ for methyl protons 3.60 ppm. Found: C, 81.42; H, 5.24%.

mixture of methanol and water (2: 1 vol ratio) afforded 1.2 g (yield 8%) of *cis*-1-methyl-2-phenyl-1,2-acenaphthenediol (*cis*-**2d**) as prisms. Mp 161—162 °C, *m/e* 276 (M^+), ν_{O-H} 3300 cm^{-1}, and δ for methyl protons 1.00 ppm. Found: C, 82.25; H, 5.72%. Calcd for $C_{19}H_{16}O_3$: C, 82.58; H, 5.84%. On the other hand, the recrystallization from carbon tetrachloride of the solid obtained on evaporating the filtrate afforded 8.3 g (yield 52%) of *trans*-**2d** as white needles. Mp 111—112 °C, *m/e* 276 (M^+), ν_{O-H} 3320 and 3450 cm^{-1}, and δ for methyl protons 1.68 ppm. Found: C, 81.70; H, 5.84%.

A mixture of 3.0 g of *trans*-**2d**, 0.9 g of chromium(VI) oxide, 30 ml of acetic acid, and 9.1 ml of water was kept at 50 °C for 2 h. The reaction mixture was then poured into 70 ml of water and extracted with ether. The ethereal extract was washed with water and dried over anhydrous sodium sulfate. The red tar obtained by the evaporation of the ethereal solution under reduced pressure was solidified by treatment with a small amount of a mixture of ethyl acetate and petroleum ether. The subsequent recrystallization of the solid from 2-propanol afforded 2.8 g (yield 94%) of 1-acetyl-8-benzoylnaphthalene (**1d**) as white granules. Mp 110—111 °C, $\nu_{C=O}$ 1650 and 1680 cm^{-1}, and *m/e* 274 (M^+). Found: C, 83.26; H, 4.98%. Calcd for $C_{19}H_{14}O_2$: C, 83.19; H, 5.14%.

Conversion of ***1d*** *into 3-Phenyl-1-phenalenone.* To a DMF solution of **1d** we added a small amount of aqueous sulfuric acid or sodium hydroxide. After several minutes, the solution turned yellow. When a large amount of water was added to the solution, 3-phenyl-1-phenalenone was precipitated as yellow crystals. Mp 141—142 °C, $\nu_{C=O}$ 1630 cm^{-1}, and *m/e* 256 (M^+). Found: C, 89.39; H, 4.78%. Calcd for $C_{19}H_{12}O$: C, 89.04; H, 4.72%.

Electrolysis Procedure. An H-type electrolytic cell divided with a glass filter was used. A mercury pool (area, 12 cm^2) was used as the cathode, while the anode was a platinum disc (diameter, 2 cm). The catholyte and anolyte consisted of 60 ml of an organic solvent containing water in a concentration of 20 vol%. The supporting electrolytes were used in a concentration of 0.5 M except for sodium hydroxide, which was used in a concentration of 0.1 M. The starting diacylnaphthalene used for one run was 2.5 mmol. The catholyte was kept at 20 °C during the electrolysis, which was carried out by a controlled potential method.

Separation and Analysis of Products. General Procedure: After electrolysis, the catholyte was diluted with 300 ml of water and then neutralized with sulfuric acid or sodium hydroxide. The resulting solution was repeatedly extracted with ether, and the combined ethereal extract was dried over anhydrous sodium sulfate. The solids obtained by the evaporation of the ethereal solution were subjected to the following treatments for separation and analysis.

Electrolytic Products of ***1a***: The solid was dissolved in 30 ml of DMF, and the DMF solution was poured into 300 ml of water. When the resulting precipitate was recrystallized from ethanol, only unreacted **1a** crystallized out of the solution. The filtrate was evaporated, and the residue was recrystallized from acetic acid. The crystals thus obtained were *cis*-**2a**. The aqueous filtrate obtained at the first stage of this experiment was stored overnight in a refrigerator, and the resulting precipitate was filtered. The recrystallization of the precipitate from ethanol afforded pure *trans*-**2a**. The *cis*- and *trans*-**2a** thus obtained were identified with their authentic samples[7,9]** by mixed-melting point tests.

** The *cis* isomer (*cis*-**2a**) was also prepared using the method of Griegee.[9] Mp 174—175 °C (lit,[9] 176—177 °C) and ν_{O-H} 3220 cm^{-1}.

Electrolytic Products of ***1b***: Aliquorts of the solid obtained by the method described in *General Procedure* were subjected to NMR and IR spectroscopic analyses in order to determine the isomeric ratio of **2b** and to detect the unreacted **1b** respectively.

The unreacted **1b** was also recovered from the rest of the above solid by a method similar to that used in the case of **1a**. When the resulting isomeric mixture of **2b** was recrystallized from a small amount of aqueous methanol, *trans*-**2b** crystallized out of the solution. The crude *trans*-**2b** was recrystallized from 2-propanol. On the other hand, the recrystallization of the solids obtained by the evaporation of the methanolic filtrate from 2-propanol afforded *cis*-**2b**. The *cis*- and *trans*-**2b** thus obtained were identified with their authentic samples,†††,*** which were independently synthesized, by a mixed-melting point test.

Electrolytic Products of ***1c***: The solid obtained by the method described in *General Procedure* was dissolved in 100 ml of 0.5 M sodium hydroxide, and the resulting solution was stirred at room temperature for 12 h after the addition of 2.0 ml of dimethyl sulfate. The reaction mixture was repeatedly extracted with ether, and the combined ethereal extract was dried over anhydrous sodium sulfate. The subsequent evaporation of the etheral solution afforded methylated products‡ as white solids. These solids were analyzed much as in the case of **1b**. The methylated pinacol rearrangement product (2-phenyl-2-(4-methoxyphenyl)-1-acenaphthenone) was also detected using an IR spectroscopic method. This product was purely isolated by the use of a column chromatograph (silica gel, benzene). Mp 132—133 °C, $\nu_{C=O}$ 1720 cm^{-1}, *m/e* 350 (M^+), and δ for methyl protons 3.69 ppm. Found: C, 85.93; H, 5.05%. Calcd for $C_{25}H_{18}O_2$: C, 85.69; H, 5.18%.

Electrolytic Products of ***1d***: The solid obtained by the method described in *General Procedure* was subjected to the spectroscopic analyses of the products, and then unreacted **1d** was removed by a method similar to that used in the case of **1a** or **1b**. The recrystallization of the resulting isomeric mixture of **2d** from a mixture of methanol and water (2: 1 vol ratio) afforded *cis*-**2d**. On the other hand, the recrystallization from carbon tetrachloride of a solid obtained on evaporating the filtrate afforded *trans*-**2d**. The *cis*- and *trans*-**2d** thus obtained were identified with their authentic samples,‡‡ which were independently synthesized, by a mixed-melting point test.

The IR and NMR (90 MHz) spectra were measured in KBr tablets and in DMSO-d_6 solutions respectively, both at room temperature.

References

1) J. H. Stocker and R. M. Jenevein, *J. Org. Chem.*, **33**, 394 (1968).

2) J. H. Stocker and R. M. Jenevein, *J. Org. Chem.*, **33** 2145 (1968).

3) R. N. Gourley and J. Grimshaw, *J. Chem. Soc., C*, **1968**, 2388.

4) W. D. Hoffman, W. E. McEwen, and J. Kleinberg, *Tetrahedron*, **5**, 293 (1959).

5) T. Nonaka, A. Udagawa, and K. Odo, *Chem. Lett.*, **1975**, 2161.

*** See synthesis of 1-acyl-8-benzoylnaphthalene (**1a—d**), 1-(4-methoxybenzoyl)-8-benzoylnaphthalene (**1b**) in experimental.

‡ The products mainly consisted of **2b** and **1b**.

‡‡ See synthesis of 1-acyl-8-benzoylnaphthalenes (**1a—d**), 1-acethyl-8-benzoylnaphthalene (**1d**) in experimental.

6) J. Grimshaw and J. S. Ramsey, *J. Chem. Soc., C*, **1966**, 635.
7) E. Beschke, *Justus Liebigs Ann. Chem.*, **369**, 184 (1909).
8) J. F. McOmie and M. L. Watts, *Chem. Ind.*, **12**, 1658 (1963).
9) R. Griegee, L. Kraft, and B. Bank, *Justus Liebigs Ann. Chem.*, **507**, 195 (1933).
10) W. E. Bachmann, *J. Am. Chem. Soc.*, **54**, 1969 (1932).
11) P. D. Bartlett and R. F. Brown, *J. Am. Chem. Soc.*, **62**, 2927 (1940).
12) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley & Sons, New York (1964), p. 95.
13) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York (1967), p. 55.
14) P. Zuman, D. Barns, and A. Ryvolova-Kejharova, *Discuss. Faraday Soc.*, **45**, 202 (1968).
15) P. Zuman, *Collect. Czech. Chem. Commun.*, **33**, 2548 (1968).
16) In the present paper the theory of Zuman is modified in part.
17) S. Nagakura, A. Minegishi, and K. Stanfied, *J. Am. Chem. Soc.*, **79**, 1033 (1957).