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(19) The prefix *dl* is omitted from the names of racemic substances. Relative stereochemistry in cyclic systems is designated by Beilstein's system of c (cis), t (trans), and r (reference). The apparatus described by W. S. Johnson and W. P. Schneider ["Organic Syntheses", Collect. Vol. 4, Wiley, New York, N.Y., 1963, p 132] was used to maintain a nitrogen or argon atmosphere in the reaction flask. Nuclear magnetic resonance spectra were taken with either a Varian T-60, Varian CFT-20, or Hitachi Perkin-Elmer R20-B spectrometer. Nuclear magnetic resonance signals are reported as the chemical shift downfield from tetramethylsilane (Me_4Si) in parts per million of the applied field. The multiplicity of the peak is abbreviated: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). Coupling constants (*J*) are reported in hertz. High-field (270 MHz) NMR analysis was performed on selected compounds by the New England High Field Nuclear Magnetic Resonance Facility, Yale University, New Haven, Connecticut 06520.

(20) Experiments in the "**c** series" only are described in this section. A detailed account of the analogous "**a** series and **b** series" experiments is available from the Ph.D. thesis of G. A. Flynn.[13]

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Stereochemistry of the Enantioselective Electrolytic Pinacolization of α,β-Unsaturated Racemic Ketones. 2. Substituted 1,9,10,10a-Tetrahydro-3(2*H*)-phenanthrones†

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The electrochemical pinacolization of racemic ketones of the title series shows in many cases a remarkable phenomenon of enantiomeric recognition, called enantioselectivity. The relative configuration of the obtained diol (established by X-ray diffraction analysis) and the steric effects of the substituents on this selectivity indicate that the molecules are selectively absorbed on the electrode by their rear face and give information about the kind of approach of the two activated species during the pinacolization.

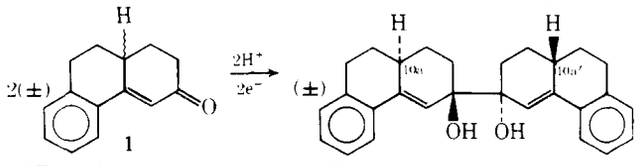
We have shown in a first paper[1] on the hydrodimerization on a mercury cathode of α,β-unsaturated, polycyclic, racemic ketones that the reaction is very selective in a number of cases. The more selective results are observed in a neutral aqueous–alcoholic medium, as in the case of the (±)-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (**1**, Scheme I).

By reduction of the corresponding resolved ketones (+)-**1** and (−)-**1**, we have found that the new C–C bond in the racemic diol appears between two like ketones. Its carbons C(10a) and C(10a′) have the same absolute configuration. Such an enantiomeric recognition has been called *enantioselectivity*.[1] A reaction between two like ketones (*R* + *R* or *S* + *S*), giving a *homodiol*, has a lower free energy of activation than a reaction between two opposite ketones (*R* + *S* or *S* + *R*), corresponding to the formation of a *heterodiol*.

Other examples of enantioselectivity are known in cases of chemical[2,3] and more particularly of electrochemical reactions in both oxidative[4] and reductive[5] processes.

In fact, the stereochemical problem of the reaction shown

Scheme I. Phenomenon of Enantioselectivity[a]



[a] Reaction is carried out at pH 6 (C_2H_5OH/CH_3COOH) with a potential (*V*) of −1.4 V on a mercury cathode.

† Originally presented at the 151st Spring Meeting of The Electrochemical Society, Inc., Philadelphia, Pa.

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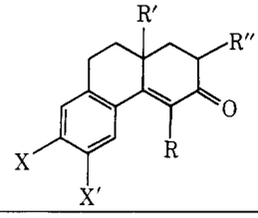
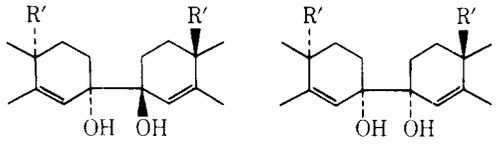
Table I. Overall Results of the Hydrodimerization of 1,9,10,10a-Tetrahydro-3(2*H*)-phenanthrones



starting ketone no.	R, R′, R″, X, X′	pH	$E_{1/2}$[a]	F/M[b]	yields, % saturated ketones	yields, % α-diols	yields, % γ-ketols
1	all H	6	0.90	0.96		79[c]	11
		11	1.32	1	6	65	1
2	R′ = CH_3	6	0.98	1.18	10	80	
		11	1.28	1.05		94	
3	R = CH_3	6	1.08	1.51	42	53	
		11	1.50	1.40	35	58	
4	R = R′ = CH_3	6	1.10	1.33	40	54	
		11	1.50	1.09	12	79	
5	R″ = CH_3	6	0.97	1.03		72[c]	18
		11	1.38	*d*	*d*	*d*	
6	X = OCH_3	6	0.98	1		74[c]	2
7	X′ = OCH_3	6	0.90	1.07		72[c]	20
8	X = OCH_3	6	1.08	1.41	40	52	
	R = CH_3	11	1.50	1.02	9	72	

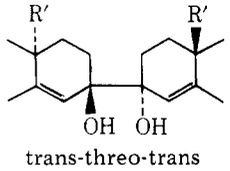
[a] Half-wave potential in volts (SCE reference). [b] Number of faradays consumed in the reduction of 1 mol of starting ketone. [c] One pure isomer. [d] Variables.[1]

Chart I. Structure and Designation of the Homodiols[a]



cis-threo-cis (c.t.c.)

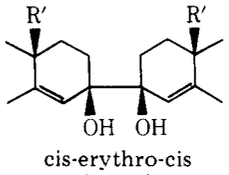
cis-erythro-trans (c.e.t.)



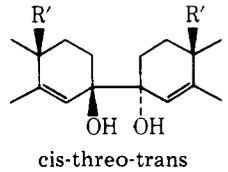
trans-threo-trans (t.t.t.)

[a] The three isomers are racemic.

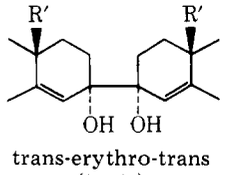
Chart II. Structure and Designation of the Heterodiols[a]



cis-erythro-cis (c.e.c.)



cis-threo-trans (c.t.t.)

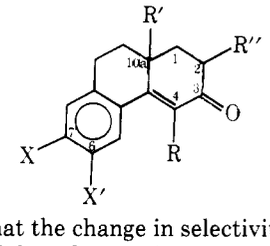


trans-erythro-trans (t.e.t.)

[a] The c.t.t. isomer is racemic, and the other two are meso.

in Scheme I is not limited to the enantiomeric recognition of the two ketones. There is also the selectivity in the stereochemistry of the two hydroxyl groups, designated by *stereoselectivity*. In Charts I and II we show the three possible isomers in each set of homo- or heterodiols. In each group, two are symmetrical (cis-cis or trans-trans), having a C_2 axis (homo series) or a mirror (hetero series), and give by proton magnetic resonance the same signal for the two halves of the molecule. The third is not symmetrical (cis-trans). In our first paper, it was established that the product of the reaction of Scheme I was a symmetrical diol of the homo series (c.t.c. or t.t.t.). Recently, we have shown by X-ray diffraction analysis[6] that it is in fact the trans-trans homodiol (trans-threo-trans isomer).

This important new stereochemical result enables us to discuss the stereochemistry of the approach of the two ketones and the importance of the electrode surface during the reaction. Thus, we have studied the reduction of a series of substituted 1,9,10,10a-tetrahydro-3(2*H*)-phenanthrones of the same series as ketone 1.

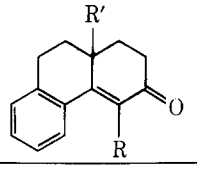


We shall see that the change in selectivity of the reaction with variations of the substrate is a very sensitive tool in the determination of the course of the reaction in each case.

Results

In Table I we have summarized the overall results of the electrochemical reduction of eight racemic ketones of the series, with various substituents, in neutral (pH 6) and basic (pH 11) media. In a number of cases, the reaction consumes more than 1 faraday per mol of starting ketone, although the formation of the α-diol (or the γ-ketol[1]) is a one-electron reduction. In these cases, we observe a large amount of saturated ketone resulting from a two-electron reduction. In all cases, the more important product of the reaction is the α-diol, which appears sometimes as a pure isomer and sometimes as a

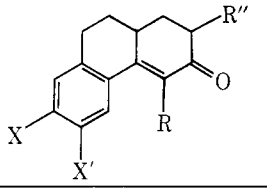
Table II. Stereochemistry of the α-Diols Resulting from the Reduction of the Following Ketones



no.	R,R′	registry no.	pH	homodiols,[a] % sym-1	homodiols,[a] % sym-2	homodiols,[a] % c.e.t.	heterodiols, % sym-1	heterodiols, % sym-2	heterodiols, % c.t.t.	E^c
1	R = R′ = H	54828-58-9	6	100[b,e]	0	0	0	0	0	1
			11	79	0	17[f]	0	0	4[g]	0.92
2	R = H	62241-77-4	6	75[d]	0	4	18	0	3	0.58
	R′ = CH_3		11	49	3	0	12	0	36	~0
3	R = CH_3	68782-26-3	6	55	2	3	4	0	36	0.4
	R′ = H		11	39	8	13	8	0	32	0.4
4	R = R′ = CH_3	63723-67-1	6	54	3	6	4	2	31	0.26
			11	22	16	6	2	2	52	−0.12

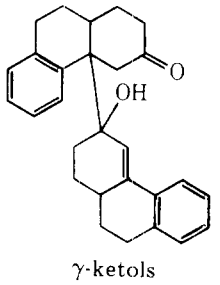
[a] These four ketones have been resolved. The homodiols are those which appear in the reduction of pure enantiomeric ketones. [b] Trans-threo-trans isomer.[6] [c] Enantioselectivity defined as $E = 1/100(\Sigma \text{ homodiols} - \Sigma \text{ heterodiols})$. [d] Tentative structures are proposed in the Discussion. [e] Registry no., 66832-52-0. [f] Registry no., 68832-53-1. [g] Registry no., 68832-54-2.

Table III. Stereochemistry of the α-Diols Resulting from the Reduction of the Nonresolved Ketones

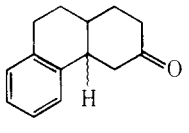


no.	R, R″, X, X′	registry no.	pH	t.t.t., %	c.t.t., %	others, %
5	R″ = CH_3		6	100	0	0
			11	100	0	0
6	X = OMe	65817-04-1	6	100	0	0
7	X′ = OMe	68782-27-4	6	100	0	0
8	X = OMe	68782-28-5	6	64[a]	36[b]	
	R = CH_3		11	44[a]	50[b]	6

[a] Assumed to be a homodiol (t.t.t. or c.t.c.). [b] Assumed to be the asymmetric heterodiol (c.t.t.). The t.t.t. structure for the diol resulting from ketones **5–7** is a tentative structure, resulting from the analogy with ketone 1 (see text).



γ-ketols



saturated ketones

mixture of four, five, or even six isomers (Tables II and III).

In these cases where the mixture of products is complex (ketones **2–4**, Table II), the starting ketones were first of all resolved[7] (as for ketone 1[8]) in order to determine which products were the homodiols and which the heterodiols. In the first case (ketone **1**), we also know by X-ray diffraction analysis that the product is the trans-trans homodiol (t.t.t.).[6] In the other cases (ketones **5–8**), we only know by NMR spectroscopy which are the symmetric isomers and which are the unsymmetrical ones (c.c.t. in the homodiol series or c.t.t. in the heterodiol series) (Table III).

In a neutral medium, when R and/or R′ are methyl groups, we observe a decrease of stereo- and enantioselectivity. In these three cases, there are two major products (Table II, pH 6). With a methyl group on the angular position (R′ = CH_3, ketone **2**), we observe a yield of 18% of a symmetrical heterodiol, probably the trans-trans isomer, as we shall later see. In the two cases where we have a methyl group on the double bond (R = CH_3, R′ = H or CH_3, ketones **3** and **4**), the results are very similar, but the heterodiol is the cis-trans isomer, formed in a yield of more than 30% (36% when R′ = H and 31% when R′ = CH_3).

In a *basic medium*, we observe another decrease in selectivity, corresponding generally to an increase in yield of one or both of the unsymmetrical diols.

We have not resolved all of the starting ketones. In three of these cases (ketones **5–7**, Table III), we observe the formation of a pure symmetrical isomer of the α-diol as in the first case. By analogy (vide infra, Discussion), we assume that this is a trans-trans homodiol (t.t.t.). In the last case (ketone **8**), the two major isomers are assumed to be a symmetrical homodiol (61 or 41% depending on the value of the pH) and the unsymmetrical heterodiol (35 or 51%) by analogy with the case of the ketone **3**. But there is a small amount of a third isomer which is a symmetrical diol (6% at pH 11).

Problem of Kinetic Control. Before undertaking the discussion of these stereochemical results, it is necessary to determine the nature of the control of the reaction. This problem has been studied in detail in the case of the four ketones of Table III. First of all, it is to be noted that the simplest and most probable mechanism of equilibration, via the tertiary allylic carbonium, cannot change the enantioselectivity of the reaction as it is the carbons 3 and 3′ which are concerned

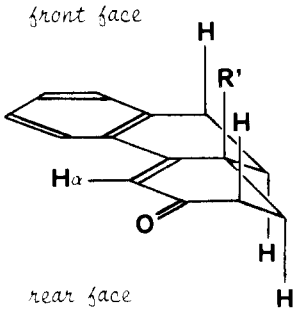
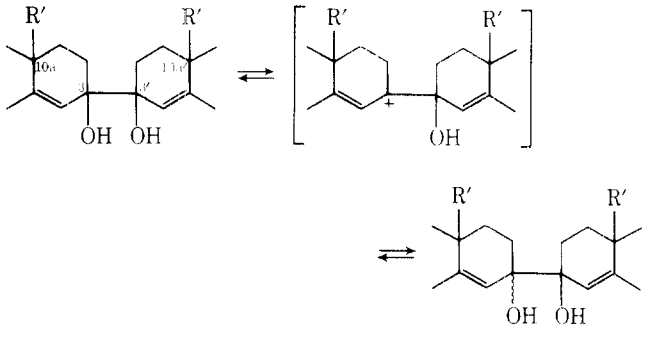


Figure 1. Steric hindrance of the front face and the rear face of ketones 1 and 2 (R′ = H or CH_3).

in the reaction and not at all carbons 10a and 10a′; a homodiol can only be transformed into another homodiol and a heterodiol into another heterodiol.



Generally, the reduction is terminated in 1 or 2 h, and, in fact, the major isomers of diol start to precipitate as soon as the current begins to pass through the solution. So, if an equilibration takes place it would have to be a very quick and efficient reaction.

To be sure that the reaction is kinetically controlled, we submitted various pure isomers of the diols issued from the ketones **1–4** to the test of equilibration during 24 h in the solvent used for the reduction.

In the case of the t.t.t. diol of ketone **1**, we observed an important dehydration with formation of the same mixture of tetraenes which was observed in acidic medium.[9] These tetraenes are a good indication of the formation of the allylic carbocation, but as they do not appear during the reaction we may say that in this first case there is no doubt that the reaction is under kinetic control.

In the case of the ketone **2**, we have observed a slow decomposition of the diols and also a slow equilibration between the isomers *sym*-**1** and c.e.t. (observed by thin-layer chromatography). We think that this equilibration is not efficient under the conditions of the reaction, all the more as there are no products of decomposition during the reduction.

The diols issued from the ketones **3** and **4** appear very stable in their saturated solutions, and thus are also cases of kinetic control.

Therefore, we may consider the results of Tables II and III as the primary products of the hydrodimerization.

Discussion

A. Pinacolization of Ketones without a Methyl Group on the Double Bond (Ketones 1, 2, 5–7). We shall begin by considering the stereochemical meaning of the trans-trans structure of the pure diol observed in the enantioselective hydrodimerization of the ketone **1** in the neutral medium.

In Figure 1 we have ketone **1** in its most probable conformation. The two sides of the molecule are not sterically equivalent. The front face has three axial hydrogens, including

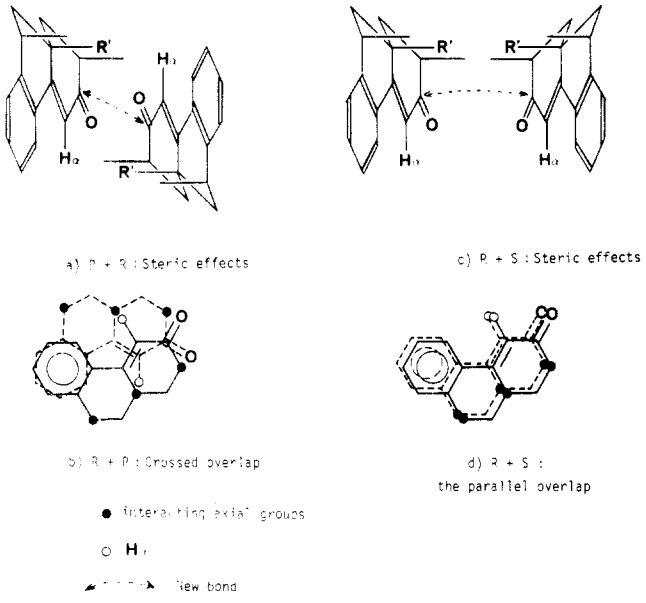


Figure 2. Formation of the trans-trans diols with a maximum overlap of the two π systems: (a) approach of two like ketones and formation of the t.t.t. homodiol with (b) the corresponding crossed overlap of the two π systems (observed reaction for ketone **1**, R′ = H); (c) approach of two opposite ketones and formation of the t.e.t. heterodiol with (d) the parallel overlap of the two π systems (unobserved reaction for ketone **1**).

the angular hydrogen R′. The rear face has only two axial hydrogens.

To explain the enantioselectivity observed in the reduction of ketone **1**, we must consider that important interactions between the skeletons of the two molecules, and an important overlap between the two π systems, occur during the reaction. In any way, it is probable that the two molecules have a tendency to approach one another face to face; otherwise it is not possible to explain the mechanism of the enantiomeric recognition. It appears that in this kind of approach interactions (and overlap) between two like ketones can be more favorable than between two opposite ketones.

In Figure 2 we see that the formation of a trans-trans diol results from the approach of the two ketones by their front face, which is apparently their most hindered face.

It is evident that the situation is very different according to whether the two ketones have the same absolute configuration (formation of the trans-trans homodiol, t.t.t.) or opposite configuration (formation of the trans-trans heterodiol, t.e.t.). Assuming a good overlap of the two π systems containing the unpaired electrons responsible for the new carbon–carbon bond, we observe that with two like ketones a good overlap can be obtained with a maximum distance, or a minimum interaction, between all of the nuclei of the two skeletons (Figure 2b, the crossed overlap). On the contrary, the approach of two opposite ketones by the front face, and with a good π overlap, implies a minimum distance or a maximum interaction between the nuclei of the two skeletons (Figure 2d, the parallel overlap). Moreover, provided that R′ is not a bulky group, the interactions between the H_α of each molecule and the three axial hydrogens (including R′) of the other in the homodiol formation (Figure 2a) appear negligible compared to the steric interactions in the heterodiol formation. In this case (Figure 2c) each axial hydrogen of one molecule is exactly directed toward its homologue on the other molecule; actually, the interactions of the axial hydrogens are maximal.

Now, let us consider the approach of two opposite ketones by opposite faces, corresponding to the formation of the cis-trans heterodiol (c.t.t.). In Figure 3 it appears that with the

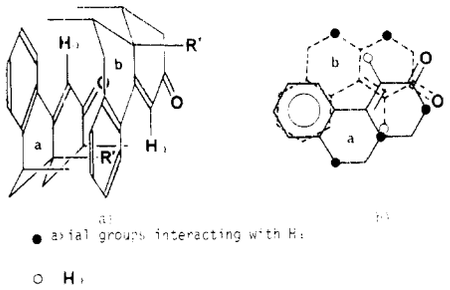


Figure 3. Formation of the cis-trans heterodiol.

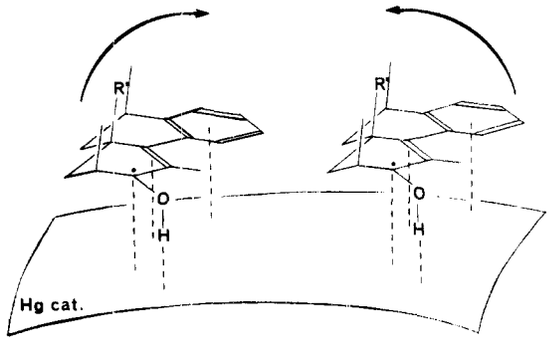


Figure 4. Formation of the trans-trans homodiol on the surface of the electrode in a neutral medium. The desorption begins by the benzene group and is achieved (after the new C–C bond has been formed) by the two hydroxyl groups. In spite of the perspective of the drawing, the motions of the two molecules are equivalent and the system is progressing toward the situation of Figures 2a,b (see also Figure 5a).

same favorable crossed overlap as in Figure 2b, we have in this case much less interaction between axial groups.

In fact, if the reaction occurs in the bulk solution,[10] this approach would be more favorable than that in Figure 2a and the formation of the cis-trans heterodiol would be prefered to the trans-trans homodiol. The same reasoning holds in the case of one molecule adsorbed on the electrode and the other one coming from the bulk solution.[11] If this assumption is true, the formation in a neutral medium of the pure trans-trans homodiol in the case of the ketone **1** indicates that the two reacting ketones are adsorbed on the electrode and that adsorption occurs very selectively by the rear face (Figure 4).

The ketone molecules are absorbed as hydroxylated radicals on the cathode by their rear face, which is the less hindered face. The unpaired electron is delocalized over all of the π system, and the molecule is absorbed quite flat on the surface of the electrode. During the formation of the new carbon-carbon bond, the unpaired electron becomes more and more localized on the hydroxylated carbon and the desorption of the molecule begins by the benzene-side of the molecule (Figure 4 or 5a). Two reactive species rotate at the surface of the electrode so as to develop an overlap between the two p atomic orbitals of the hydroxylated carbons and thus begin to orient themselves face to face. Then, we are moving toward the situation of Figure 2a, leading to the trans-trans homodiol, which is, in a neutral medium, the observed product.

If some molecules were absorbed by their front face, the situation of Figure 3 would occur, preferably leading to the cis-trans heterodiol. The selectivity of the reaction is a good indication of the selectivity of the adsorption of the ketone (or of the intermediate hydroxylated radical) by the rear face.

This mechanism is very similar to that described by Bobbitt[4] for the oxidative dimerization of phenols (Scheme II). The most important difference is that in our case, in a neutral medium, the ketone is adsorbed at the surface of the cathode

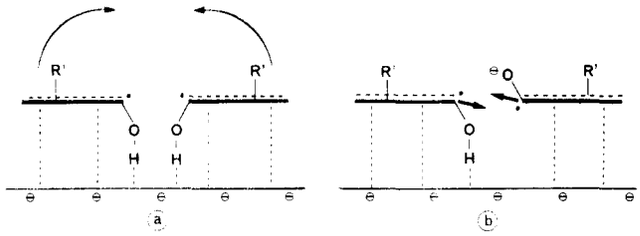
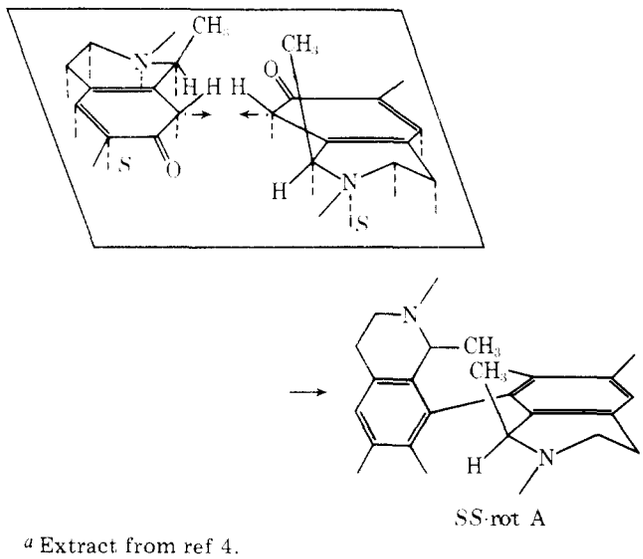


Figure 5. Stereochemistry of the pinacolization in a basic medium: (a) meeting of two hydroxylated radicals, leading to the same product as in neutral medium; (b) meeting of a hydroxylated radical and an anionic radical, leading to the cis-trans diols (structure cis corresponding to the anionic part). As the medium is not too basic, the concentration of anionic species on the cathode is low and the formation of cis-cis homo- or heterodiols, resulting from the meeting of two such species, does not occur with high yields.

Scheme II[a]



[a] Extract from ref 4.

as a hydroxylated radical with its hydroxyl group directed toward the electrode, leading to the trans-trans structure of the observed diol.

Another interesting analogy is that Bobbitt observed that the oxidative dimerization of phenols is more selective in a basic medium, the explanation being that in such a medium the intermediate radical has a charged phenate group and is more strongly adsorbed on the anode. In our case, the reaction occurs on the cathode and a ketone, adsorbed as a negatively charged alcoholate radical, will be less strongly adsorbed. In fact, we always observe a decrease in selectivity when the medium is basic (pH 11). A first explanation would be that in a basic medium the reaction occurs between two desorbed intermediate species or between one adsorbed and one desorbed species. With this explanation, the cis-trans heterodiol (c.t.t.) would be the most important new diol (Figure 3). This is not the case. We observe (1) only 4% of the expected c.t.t. unsymmetrical heterodiol and 17% of the c.e.t. unsymmetrical homodiol. We think that in such slightly basic medium almost all of the molecules are adsorbed as hydroxylated radicals (as in Figure 4, for the neutral medium) and only a few molecules are adsorbed as anionic radicals. In this case (Figure 5a), the alcoholate group is directed away from the electrode and the meeting of a hydroxylated radical and an anionic radical leads to a cis-trans diol (Figure 5) with neither rotation of the species nor frontal approach and thus without selectivity. In fact, with ketone **1** we observe 17% of the c.e.t. homodiol and only 4% of the c.t.t. heterodiol, while with ketone **2** we observe

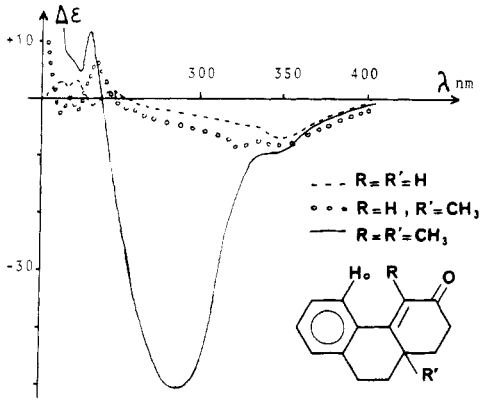


Figure 6. Influence of a methyl group on the double bond (R) on the rotational strength of the tetrahydro-1,9,10,10a-3(2*H*)-phenanthrones.

Table IV. Effect of Methyl Group on the UV Spectrum of Ketones 3 and 4

ketone 1	λ_{max} (EtOH) = 298 nm (ϵ 20 500)
ketone 3	λ_{max} (EtOH) = 287 nm (ϵ 19 000)
	λ_{calcd} = 298 + 10 = 308 nm, $\Delta\lambda$ = −21 nm
ketone 2	λ_{max} (EtOH) = 296 nm (ϵ 21 200)
ketone 4	λ_{max} (EtOH) = 289 nm (ϵ 18 000)
	λ_{calcd} = 296 + 10 = 306 nm, $\Delta\lambda$ = −17 nm

36% of the c.t.t. heterodiol and only 3% of the c.e.t. homodiol at pH 11.

The case of the ketone **5**, which gives the same selectivity (100% t.t.t.) in neutral and basic media, is interesting. The methyl group in R″ is equatorial in the neighborhood of the carbonyl group as it seems by solvent effect in NMR spectroscopy: δCH_3 (CCl_4) = 1.10 ppm, δCH_3 (C_6D_6) = 1.2 ppm, $\Delta\delta = \delta(CCl_4) - \delta(C_6D_6)$ = +0.10 ppm. So, it is probable that this methyl group strains the lateral approach shown in Figure 5b and hinders the formation of the cis-trans diols.

Otherwise, the behavior of ketones **5–7** (Table III), having no substituents in the R and R′ positions, is very similar to that of the ketone 1 in the neutral medium: 100% of a pure symmetrical diol, which is probably the trans-trans homodiol. Neither a methoxy group on the benzene system (conjugated **6** or not conjugated **7** to the carbonyl group) nor an equatorial methyl in the C_2 position (ketone **5**) introduces any new important interaction or effect in the frontal approach.

It is more difficult to explain the result for ketone **2** at pH 6 (Table II). With an angular methyl group in R′, the adsorption by the rear face is even more selective than with the ketone **1**, but the frontal approach as in Figure 2a is strained by the interactions of R′ = CH_3 and H_α. It is probable that in this case another kind of approach becomes competitive with the mechanism of Figure 4 or 5a which continues to give in the homodiol series the trans-trans isomer (probably an important part of the 75% of the major product, which is a symmetrical homodiol as demonstrated by pinacolization of the optically active ketone (+)-**2** and by NMR spectroscopy). Therefore, we think that the major product (Table II), *sym*-**1** homodiol, is a trans-trans isomer (t.t.t. 75%). As the adsorption is probably very selective, we think also that the *sym*-**1** observed heterodiol (18%) is also a trans-trans isomer (t.e.t.). Perhaps the unsymmetrical heterodiol observed with ketone **2** at pH 11 is a product with only one adsorbed molecule, as in Figure 3, the radical anion species being desorbed. The increasing

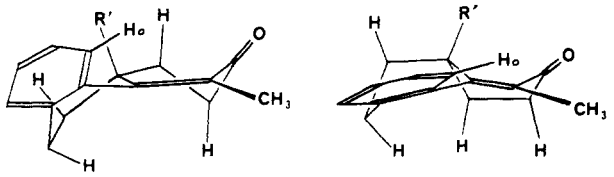


Figure 7. Possible conformations for 4-substituted tetrahydro-1,9,10,10a-3(2*H*)-phenanthrones.

difficulty of approach of the two activated species probably explains the increase of saturated ketone (10% for ketone **2**, while 0% for ketone **1**) (Table I).

B. Pinacolization of Ketones Having a Methyl on the Double Bond (Ketones 3, 4, 8). With a methyl group on the double bond, the formation of a large amount of the cis-trans heterodiol (36% in the neutral medium for the ketone **3**) indicates a nonselective adsorption. We observe that in this case, the selectivity of the hydrodimerization is very low and that a methyl in the angular position (ketone **4**) leads to about the same result. Thus, we must ask ourselves why a methyl group on the double bond increases the hindrance of the rear face, making the influence of the angular substituent negligible.

In fact, this methyl group interacts strongly with the ortho hydrogen and the UV spectra (Table IV) show an important blue shift of −20 nm, indicating a loss of conjugation and an important change in the geometry of the molecule. Even more surprising is the change in the circular dichroism curves. When R = H, the π to π^* transition has a very low rotational strength. With a methyl on the double bond, a phenomenal increase of this rotational strength appears (Figure 6). This also indicates a change of molecular geometry.

With the molecular stereomodels, a good release of the compression between H_o and the methyl can be obtained in the conformations of Figure 7 for instance. But the methyl group is always directed toward the rear face, making the adsorption of the molecules by this face less selective.

It is also possible that in the case of well-conjugated ketones such as **1** or **2**, the intermediate hydroxylated radical has a half-life long enough to be adsorbed and desorbed at the surface of the electrode many times and thus reaches an equilibrium of adsorption by the rear face only. In the case of ketones **3** or **4**, the intermediate radical is not well conjugated and perhaps the last step of the reaction is performed before this equilibrium at the surface of the electrode is reached. In any way, the molecule is no longer flat enough to be strongly absorbed on the cathode by all of its surface (including the benzene ring[12]) and the increase of the cis-trans heterodiol may result from the reaction with only one adsorbed species.

All of these reasons explain very well the loss of selectivity observed during the hydrodimerization of ketones **3**, **4**, or **8**.

Conclusion

In conclusion, we see that the stereochemistry of the pinacolization of 1,9,10,10a-tetrahydro-3(2*H*)-phenanthrones on a mercury cathode gives some interesting information about the stereochemical processes on the electrode.

Firstly, it seems that in this case *both molecules are adsorbed* on the cathode, and this is an interesting example of an electron-rich system closely adsorbed on the cathode, in spite of its negative character.

Secondly, if this assumption is true, we should have information about *the selectivity and the strength of this adsorption*, as we have observed a case of trans-trans homodiol, corresponding to a selective adsorption by the rear face (ketone **1**), and cases of cis-trans heterodiol with poor and nonselective adsorption (ketones **3** or **4**).

Hence, we see that different *kinds of approaches* of two molecules at the surface of the electrode are possible, depending on the hindrance of the R and R′ groups, and on the pH of the medium.

Experimental Section

General Procedure. The reductions were performed in a two-compartment cell separated by a fritted glass disk at room temperature using a mercury cathode and a SCE reference electrode. Pure nitrogen was continuously bubbled into the cathodic compartment. Two different electrolytic mother solutions have been used depending on the wanted pH: a solution of acetic acid (2 M) and potassium acetate (1 M) for neutral medium (pH 6), and a solution of 0.2 M KOH for basic medium (pH 11). The ketones were dissolved in ethanol (2.5 g in 100 mL), and the solution for electrolysis was obtained by mixing one part of the electrolytic mother solution with four parts of the ethanol solution of the ketone.

The potential was controlled to ±0.05 V. The initial current of about 200 mA fell to 5 mA over a period of 4–6 h. This current was integrated electronically during the reaction. Generally, a precipitate appeared during the electrolysis. Filtration gives an insoluble fraction which was analyzed by TLC (thin-layer chromatography) and NMR spectroscopy. The solution was extracted with ether, and after evaporation at room temperature the residue was analyzed in the same way.

The TLC was carried out on silica gel (PF 254 + 366) using variable mixtures of light petroleum and moist ether as eluting solvent. Each fraction obtained by TLC was analyzed by NMR spectroscopy.

The reduction of the optically active ketone gave us the means to distinguish the three homodiols; the unsymmetrical homodiol was then known with certainty (c.t.t.) by NMR, and the structures of the two symmetrical homodiols were established by X-ray diffraction or by analogy with the first one (tentative structure between t.t.t. and c.t.c.). The diols which appear in the reduction of the racemic ketones (and which are not homodiols) are the heterodiols; the unsymmetrical one is known with certainty (c.e.t.), and two symmetrical diols are t.e.t. or c.e.c. (tentative structure).

Reduction of 10a-Methyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (2). Active Ketone (+)-2, pH 11. The reduction at pH 11 ($V = -1.7$ V) of a solution of 280 mg of the active ketone (+)-**2** gave a precipitate of 220 mg of the pure crystallized (+)-trans-threo-trans (t.t.t.) diol. By TLC, we separated from the residual solution (40 mg) a crystallized fraction containing two diols in equal amounts: the same isomer as above and the asymmetric cis-erythro-trans (c.e.t.) isomer.

(+)-Trans-threo-trans isomer: $[\alpha]^{25}_{589}$ +51° (*c* 0.5, pyridine) (*sym*-**1** homodiol); mp 257 °C dec; IR (KBr) ν_{OH} 3650, 3520, 3420 cm^{-1}; NMR ($CDCl_3$ + Me_2SO) $\delta H_4 = \delta H_{4'} = 6.30$ ppm (s), $\delta OH = \delta OH' = 4.35$ ppm (s), $\delta CH_3 = 0.97$ ppm (s).

Cis-erythro-trans isomer (the unsymmetrical homodiol): NMR ($CDCl_3$, Me_2SO) $\delta H_4 = 6.25$ ppm (s), $\delta H_{4'} = 6.13$ ppm (s), $\delta OH = 4.23$ ppm (s), $\delta OH' = 4.13$ ppm (s), $\delta CH_3 = 1.00$ ppm (s), $\delta CH_3' = 0.97$ ppm (s).

Racemic Ketone (±)-2, pH 6. The reduction at pH 6 ($V = -1.4$ V) of a solution of 3.2 g of the racemic ketone (±)-**2** gave 1.7 g of the insoluble (±)-t.t.t. diol (mp = 221 °C dec). In spite of a lower melting point than for the (+)-t.t.t. isomer, this is not a conglomerate (IR spectra in KBr are not exactly the same). From the solution we separated by TLC three fractions containing (decreasing R_f values) 320 mg of a saturated ketone (mp = 72 °C), 255 mg of a mixture of the two diols (±)-t.t.t. and (±)-c.t.t. in a 7:3 ratio, and 570 mg of a mixture of two other diols [*sym*-1 heterodiol, a meso isomer (t.e.t.), and (±)-c.e.t. in a 4:1 ratio].

(±)-Cis-threo-trans isomer (the unsymmetrical heterodiol): NMR $\delta H_4 = 6.35$ ppm (s), $\delta H_{4'} = 6.25$ ppm (s), $\delta OH = 4.37$ ppm (s), $\delta OH' = 4.20$ ppm (s), $\delta CH_3 = 0.97$ ppm (s), $\delta CH_3' = 0.85$ ppm (s).

Trans-erythro-trans isomer (*sym*-**1** heterodiol): NMR $\delta H_4 = 6.10$ ppm (s), $\delta OH = 4.35$ ppm (s), $\delta CH_3 = 0.93$ ppm (s).

Racemic Ketone (±)-2, pH 11. The reduction at pH 11 ($V = -1.7$ V) of 2.5 g of the racemic ketone (±)-**2** gave 1.7 g of an insoluble mixture of two diols, (±)-t.t.t. and (±)-c.t.t., in a 16:9 ratio. From the solution, we obtained by TLC (R_f decreasing values) 280 mg of (±)-t.t.t. and c.t.t. (1:4 ratio) and 360 mg of t.e.t. and (±)-c.e.t. (3:1 ratio).

Reduction of 4-Methyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (3). Homodiols are known by reduction (pH 11) of the partially resolved (+)-ketone.

Racemic Ketone (±)-3, pH 6. The reduction at pH 6 of 2.5 g of the racemic ketone (±)-**3** (−1.5 V) gave a mixture of 1.150 g of two insoluble diols, (±)-t.t.t. ($\delta OH = 4.5$ ppm) (*sym*-**1** homodiol) and (±)-c.t.t. (5.10 and 4.80 ppm) (the unsymmetrical heterodiol), in an 8:5 ratio. By TLC, we separated from the solution 1.050 g of a mixture of saturated ketones, 75 mg of a mixture of the three diols (±)-t.t.t., (±)-c.t.c. ($\delta OH = 5.03$ ppm) (*sym*-**2** heterodiol), and (±)-c.t.t. (1:1:1 ratio), and 100 mg of a mixture of the two diols (±)-c.e.t. ($\delta OH = 4.30$ ppm, $\delta CH_3 = 2.00$ and 2.27 ppm) (the unsymmetrical homodiol) and *meso*-t.e.t. ($\delta OH = 4.00$ ppm) (*sym*-**1** heterodiol) (2:3 ratio).

Racemic Ketone (±)-3, pH 11. The reduction of 2 g of the racemic ketone (±)-**3** at pH 11 (−1.8 V) gave 850 mg of a mixture of three insoluble diols, (±)-t.t.t., (±)-c.t.c., and (±)-c.t.t., in a 6:1:5 ratio. In the solution, we found by TLC 700 mg of a mixture of saturated ketones, 70 mg of a mixture of (±)-t.t.t. and (±)-c.t.c. diols in a ratio of 7:3, and 250 mg of a mixture of (±)-c.e.t. and *meso*-t.e.t. diols in a ratio of 5:4.

Reduction of 4,10a-Dimethyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (4). Dextrorotatory Ketone (+)-4, pH 6. The reduction at pH 6 (1.5 V) of 200 mg of the ketone (+)-**4** was carried out. There was no precipate formed. By TLC we separated from the solution 82 mg of a mixture of saturated ketones, 85 mg of the pure (+)-t.t.t diol (*sym*-**1** homodiol), and 14 mg of the pure (+)-c.e.t. diol (the unsymmetrical homodiol).

(+)-Trans-threo-trans isomer: $[\alpha]^{25}_{589}$ +573° (*c* 0.45, pyridine); mp 120 °C dec; IR (KBr) ν_{OH} 3450 cm^{-1}; NMR (Me_2SO + $CDCl_3$) $\delta OH = 4.60$ ppm (s), $\delta CH_3(10a) = 0.83$ ppm (s), $\delta CH_3(4) = 1.97$ ppm (s).

In acetonitrile this isomer gave beautiful monoclinic single crystals (space group $P2_1$ with $Z = 4$, $\beta = 98.66°$, $a = 15.788$ Å, $b = 12.063$ Å, and $c = 14.235$ Å). There are two molecules per asymmetric unit in the unit cell. So there are many difficulties in the refinement of its structure.

(+)-Cis-erythro-trans isomer: $[\alpha]^{25}_{578}$ +230° (*c* 0.45, pyridine); IR (film) ν_{OH} 3430 cm^{-1}; NMR $\delta OH = 4.27$ ppm (s), $\delta CH_3(4) = 2.08$ ppm, $\delta CH_3(4') = 1.70$ ppm, $\delta CH_3(10a) = 0.67$ ppm, $\delta CH_3(10a') = 0.77$ ppm.

Dextrorotatory Ketone (+)-4, pH 11. The reduction at pH 11 (−1.8 V) of 240 mg of the same (+)-**4** ketone gave a precipitate (130 mg) of two insoluble diols, t.t.t. and c.t.c. ($\delta OH = 4.97$ ppm), in a ratio of 4:3. From the solution, we isolated by TLC 40 mg of saturated ketones, 25 mg of a mixture of the two diols t.t.t. and c.t.c. in a 3:2 ratio (*sym*-**1** and *sym*-**2** homodiols), and 25 mg of the pure c.e.t. diol.

Racemic Ketone (±)-4, pH 6. Reduction of 2.5 g of the racemic ketone (±)-**4** at pH 6 (−1.5 V) gave 730 mg of the pure (±)-t.t.t. diol. By addition of light petroleum and ether to the solution, we obtained 250 mg of another pure insoluble diol, (±)-c.t.t. From the latter solution we separated by TLC 1 g of saturated ketones, 240 mg of a mixture of the three diols (±)-c.t.t., (±)-c.t.c., and *meso*-c.e.c. (*sym*-**2** heterodiol) in a 19:4:3 ratio, and 135 mg of a mixture of two other diols [(±)-c.e.t. and *meso*-t.e.t. (*sym*-**1** heterodiol) in a 3:2 ratio].

(±)-Trans-threo-trans isomer: mp 204 °C dec; IR (KBr) 3490 and 3370 cm^{-1}; NMR (Me_2SO + $CDCl_3$) $\delta OH = 4.60$ ppm.

(±)-Cis-threo-trans isomer: mp 198 °C dec; IR (KBr) 3490 and 3350 cm^{-1}; NMR (Me_2SO + $CDCl_3$) $\delta OH = 5.17$ and 4.77 ppm, $\delta CH_3(10a) = 0.87$ and 0.80 ppm, $\delta CH_3(4) = 2.0$ ppm.

(±)-Cis-threo-cis isomer: NMR (Me_2SO + $CDCl_3$) $\delta OH = 5.0$ ppm.

(±) Cis-erythro-trans isomer: NMR (Me_2SO + $CDCl_3$) $\delta OH = 4.27$ ppm (the two hydroxyl groups have the same chemical shift), $\delta CH_3(4) = 2.08$ and 1.70 ppm, $\delta CH_3(10a) = 0.77$ and 0.67 ppm.

Meso trans-erythro-trans isomer: NMR (Me_2SO + $CDCl_3$) $\delta OH = 3.97$ ppm.

Meso cis-erythro-cis isomer: NMR (Me_2SO + $CDCl_3$) $\delta OH = 4.60$ ppm. In spite of having the same chemical shift as the t.t.t. isomer, these last two products are different, having different R_f values.

Racemic Ketone (±)-4, pH 11. The reduction of 2.5 g of the racemic ketone (±)-**4** at pH 11 (−1.7 V) gave a precipitate of 1.690 g of three insoluble diols, (±)-t.t.t., (±)-c.t.t., and (±)-c.t.c., in a 6:13:4 ratio. The soluble part was separated by TLC and gave 300 mg of one pure saturated ketone, 130 mg of a mixture of the three diols (±)-t.t.c., (±)-c.t.c., and *meso*-c.e.c. in a 6:3:4 ratio, and 160 mg of a mixture of the two diols (±)-t.e.c. and *meso*-t.e.t. in a 3:1 ratio.

Reduction of 2-Methyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (5). This reduction has been described.[1]

Reduction of 7-Methoxy-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (6). The reduction of 2.5 g of the racemic ketone (±)-**6** at pH 6 (−1.4 V) gave 1.85 g of the pure insoluble (±)-t.t.t. diol: mp = 242 °C dec; $\delta OH = 4.33$ ppm, $\delta CH_3O = 3.70$ ppm; ν_{OH} 3430 and 3260 cm^{-1} (KBr). The other products decomposed during TLC separation. In fact, there are three other compounds which are probably not diols as they do not give the characteristic green coloration with sulfuric acid which is observed with all other diols when R(4) = H. These three

products are two γ-ketols (or their hemiketal cyclic forms) and a ketone resulting from their decomposition.

Reduction of 6-Methoxy-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (7). The reduction of 2.5 g of the racemic ketone (±)-**7** at pH 6 (−1.4 V) gave 1.6 g of a pure crystallized diol, (±)-t.t.t. isomer. (±)-Trans-threo-trans isomer (tentative structure): mp 140 °C dec; IR (KBr) ν_{OH} 3410 cm^{-1}; NMR (Me_2SO + $CDCl_3$) δCH(4) = 6.47 ppm, δOH = 4.33 ppm, δCH_3 = 3.57 ppm.

From the solution we obtained two fractions: 300 mg of a pure γ-ketol [mp = 160 °C; ν_{OH} 3650 and 3490, $\nu_{C=O}$ 1715 cm^{-1} (KBr); NMR ($CDCl_3$ + Me_2SO) δCH(4) = 6.32 ppm, δCH_3 = 3.77 and 3.80 ppm, δOH = 3.60 ppm] and 400 mg of a mixture of the t.t.t. diol (100 mg of which was separated by crystallization in ether) and two ketols in an 8:2 ratio, characterized by their NMR spectra (δCH = 5.58 ppm, δOH = 3.93 ppm and δCH = 6.20 ppm, δOH = 3.62 ppm, respectively).

Reduction of 7-Methoxy-4-methyl-1,9,10,10a-tetrahydro-3(2*H*)-phenanthrone (8). Racemic Ketone (±)-8, pH 6. The reduction of 2.5 g of the racemic ketone (±)-**8** at pH 6 (−1.5 V) gave 1.1 g of a crystallized mixture of the two diols (±)-t.t.t. (tentative structure) (δOH = 4.53 ppm) and (±)-c.t.t. (δOH = 5.07 and 4.73 ppm) in a 13:7 ratio. From the mother solution, we obtained by TLC 1 g of a mixture of saturated ketones, 190 mg of (±)-t.t.t. and (±)-c.t.c. diols in a 11:9 ratio, and 50 mg of a complicated mixture.

Racemic Ketone (±)-8, pH 11. The reduction of 2.7 g of the racemic ketone (±)-**8** at pH 11 (−1.7 V) gave a mixture of two insoluble diols (2 g), (±)-t.t.t. and (±)-c.t.t. (tentative structures), in a 9:11 ratio. By TLC of the residue, we separated 240 mg of a mixture of saturated ketones and three fractions (140, 50, and 240 mg) containing ketonic products (IR). By crystallization, we obtained 70 mg of the (±)-t.t.t. diol (mp = 203 °C dec; ν_{OH} (KBr) 3520 and 3370 cm^{-1}) and 120 mg of another symmetric diol (mp = 174 °C dec; ν_{OH} 3525 and 3510 cm^{-1}; δOH = 3.97 ppm, δCH_3(OMe) = 3.7 ppm, δCH_3(4) = 2 ppm).

Registry No.—(±)-**2**, 63783-22-2; (+)-**2** pinacol deriv., t.t.t. isomer, 68782-29-6; (+)-**2** pinacol deriv., c.e.t. isomer, 68832-55-3; (±)-**2** pinacol deriv., t.t.t. isomer, 68832-56-4; (±)-**2** pinacol deriv., c.t.t. isomer, 68832-57-5; (±)-**2** pinacol deriv., t.e.t. isomer, 68832-58-6; (±)-**2** pinacol deriv., c.e.t. isomer, 68832-59-7; (±)-**3**, 68782-30-9; (±)-**3** pinacol deriv., t.t.t. isomer, 68782-31-0; (±)-**3** pinacol deriv., c.t.c. isomer, 68832-60-0; (±)-**3** pinacol deriv., c.t.t. isomer, 68832-61-1; (±)-**3** pinacol deriv., c.e.t. isomer, 68832-62-2; (±)-**3** pinacol deriv., t.e.t. isomer, 68832-63-3; (±)-**4**, 68782-32-1; (+)-**4** pinacol deriv., t.t.t. isomer, 68782-33-2; (+)-**4** pinacol deriv., c.e.t. isomer, 68832-64-4; (+)-**4** pinacol deriv., c.t.c. isomer, 68832-65-5; (±)-**4** pinacol deriv., t.t.t. isomer, 68832-66-6; (±)-**4** pinacol deriv., c.t.t. isomer, 68832-67-7; (±)-**4** pinacol deriv., c.t.c. isomer, 68832-68-8; (±)-**4** pinacol deriv., c.e.c. isomer, 68832-69-9; (±)-**4** pinacol deriv., c.e.t. isomer, 68832-70-2; (±)-**4** pinacol deriv., t.e.t. isomer, 68832-71-3; (±)-**6** pinacol deriv., t.t.t. isomer, 68782-34-3; (±)-**7** pinacol deriv., t.t.t. isomer, 68813-13-8; (±)-**8** pinacol deriv., t.t.t. isomer, 68782-35-4; (±)-**8** pinacol deriv., c.t.t. isomer, 68832-72-4; (±)-**8** pinacol deriv., c.t.c. isomer, 68832-73-5; 1,2,3,4,4a,9,10,10a-octahydro-10a-methyl-3-phenanthrenone, 68782-36-5; 1,2,3,4,4a,9,10,10a-octahydro-4-methyl-3-phenanthrenone, 68782-37-6; 1,2,3,4,4a,9,10,10a-octahydro-4,10a-dimethyl-3-phenanthrenone, 68782-38-7; 1,1′,2,3,9,9′,10,10′,10a,10a′-decahydro-3-hydroxy-6,6′-dimethoxy[3,4a′(2′*H*)-biphenanthren]-3′(4′-*H*)-one, 68782-39-8; 1,2,3,4,4a,9,10,10a-octahydro-4-methyl-7-methoxy-3-phenanthrenone, 68782-40-1.

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Synthetic Electrochemical Studies on Nucleosides. 1. Novel Method for the Synthesis of 2′,3′-Unsaturated Nucleosides via Electrolysis

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A novel method for the synthesis of 2′,3′-unsaturated nucleosides via electrochemical reductions of 2′(3′)-*O*-acyl-3′(2′)-deoxyhalonucleosides is described. Electrolysis of 9-(2,5-di-*O*-acetyl-3-bromo-3-deoxy-β-D-xylofuranosyl)adenine (**1a**) at −1.3 V vs. SCE in MeOH–AcONa (0.25 M) gave 9-(5-*O*-acetyl-2,3-dideoxy-β-D-*glycero*-pent-2-enofuranosyl)adenine (**2a**) in 76% yield. The compound **2a** was also obtained in 74% yield via electrolysis of a positional isomer **1b**, 9-(3,5-di-*O*-acetyl-2-bromo-2-deoxy-β-D-arabinofuranosyl)adenine, under the same conditions. This electrochemical method could be extended to the synthesis of pyrimidine nucleosides (**2b** and **2c**) using tetraethylammonium tosylate as an electrolyte in DMF solution. In the electrolysis of **1f** in MeOH–AcONa (0.25 M), however, the extensive glycosidic cleavage followed by the formation of methyl 5-*O*-propionyl-2,3-dideoxy-D-*glycero*-pent-2-enofuranoside (**6**), furfuryl propionate (**7**), and uracil was observed, and **2c** was obtained in only 38% yield. This glycosidic cleavage provides the first example of an electrochemical elimination of a halogen and an adjacent substituent bonded via a nitrogen atom. 3′-Deoxyadenosine (cordycepin) was obtained in 14% yield together with **3a** (29%) and adenine (55%) via the electrolysis of 9-(3-deoxy-3-iodo-β-D-xylofuranosyl)adenine (**1d**) in MeOH–AcONa (0.25 M).

Electrochemical studies on nucleosides and nucleotides have been reported by a number of investigators.[1] These studies have been almost exclusively focused on reduction or oxidation of the nucleic acid bases by using polarography and related techniques, e.g., cyclic voltammetry,[1b,h] alternating current polarography,[1a,f] and oscillographic polarography,[1a] and little attention has been paid to the synthetic application of electrochemical techniques to the nucleoside field except in a few instances.[2] Electrolysis can be carried out in neutral media (protic or aprotic) at temperatures ranging from ambient or higher to well below 0 °C, and controlled potential electrolysis makes possible selective reaction of very similar

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