The Anodic Reaction of (S)-2-Acetamido-2-(3,4-dimethoxybenzyl)propionitrile. Synthetic and Stereochemical Implications

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Reaction of the title compound **1** at a Pt anode (1.14 V *vs.* sce) in sodium acetate–acetic acid containing acetic anhydride gives (4*R*,5*S*)- and (4*R*,5*R*)-4-cyano-5-(3,4-dimethoxyphenyl)-2,4-dimethyl-2-oxazoline (**3** and **4**), respectively, in a 3.5:1 ratio as the major products. This stereoselectivity results not from the heterogeneity of reaction of adsorbed species *on* an anode surface, but from the nature of benzylic cation **2**, since the same oxazolines are formed in the homogeneous reaction of **1** with $Mn(OAc)_3$ in similar ratio. Lesser products of reaction, most of which derive from benzylic oxidation, are considered. The hydrolysis of some of them is examined insofar as it bears on stereochemical correlations and reaction work-up.

It has come to mind that the anodic side chain acetoxylation reaction[1] could provide a new means of introducing an oxygen function into a β-arylalanine derivative to form a β-arylserine derivative.

Exploration of this reaction could provide additional benefit. Most of the studies of anodic side chain oxidation have been carried out on reasonably simple molecules, and the majority of them have been concerned with unraveling the mechanism of electron transfer.[1,2] This basic question is now well answered,[3] but experiments on the possible stereochemical consequence of reaction at a solid anode surface are few, and it seemed that some contribution to this important facet of electroorganic chemistry might result.

Eberson previously expressed the hope[4] that stereochemical studies would illustrate some differences between anodic acetoxylation and mechanistically similar electrophilic processes which could be attributed to the heterogeneous nature of the electrode surface. Our substrate for such an electrolysis, (*S*)-2-acetamido-2-(3,4-dimethoxybenzyl)propionitrile[5] (**1**), not only possessed a chiral center, but the differing polarizability of the attached groups suggested that the different conformers might contribute an effect somewhat different from a solely steric one.

Results and Discussion

(*S*)-2-Acetamido-2-(3,4-dimethoxybenzyl)propionitrile (**1**) was allowed to react at a platinum mesh electrode in acetic acid–sodium acetate containing acetic anhydride under controlled potential conditions (1.14 V *vs.* sce). The major products resulted from an ece-formed benzylic cation,[2-4] and are shown in Chart I with their correct stereochemical representation. These configurations imply that no changes occurred at the original chiral center. The two major products, (4*R*,5*S*)-4-cyano-5-(3,4-dimethoxyphenyl)-2,4-dimethyl-2-oxazoline (**3**) and its diastereomeric 4*R*,5*R* isomer, **4**, were formed in a ratio of about 3.5:1 as judged from nmr integrals. The products of acetate attack, (2*R*,3*S*)-3-acetoxy-2-acetamido-3-(3,4-dimethoxyphenyl)-2-methylpropionitrile (**6**), its 2*R*,3*R* isomer, **7** (not shown), and (4*R*,5*S*)-5-acetoxy-4-cyano-5-(3,4-dimethoxyphenyl)-2,4-dimethyl-2-oxazoline (**8**), amplify the nature of the reactions occurring, especially since **8** is the formal product of two cation formations.

Products **4**, **7**, and **8** were not isolated in pure form, but their presence was amply demonstrated in partially purified fractions by spectral methods and by hydrolysis (of **4** and **8**) to rational, fully characterized, crystalline products (see below).

Aliquots which were analyzed throughout the electrolysis gave results in harmony with the isolations performed at the conclusion of the run. Integrals of the nmr (see Figure 1) permitted product estimation as follows.

Product	Approx conversion, %[a]
3	40
4	11
6 and **7**	7.5
8	5

[a] Based on **1** charged.

That the true "acetoxylation" products, **6** and **7**, were found in lower yield than the oxazolines, **3** and **4**, is not surprising in view of the proximity of the amide oxygen for attack in cation **2**.[6] The diastereomer of **8** was not found. Intuitively, one would expect **3** to be adsorbed on the anode more readily than **4**, because both the aromatic ring and the polarizable nitrile are cis. Acetoxylation *at the anode* would give the isomer *not* observed. With such a highly stabilized cation as **5**, however, diffusion to the bulk solution can be expected where the veratryl ring would tend toward coplanarity and acetate attack would occur from the less hindered side to give **8**. Such attack might not, however, be predicted to be exclusive.

A small amount (less than 1%) of 3,4-dimethoxybenzaldehyde (**9**)[8] was invariably formed. From some electrolyses, at slightly higher potential, it was pos-

(1) L. Eberson and H. Schäfer, "Organic Electrochemistry," Fortscritte der Chemischen Forschung, No. 21, Springer-Verlag, New York, N. Y., 1971. Chapters 7 and 9 are particularly pertinent.

(2) V. D. Parker and R. N. Adams, *Tetrahedron Lett.*, 1721 (1969).

(3) For a less sanguine view, see A. Bewick and D. Pletcher in "Electrochemistry," Vol. 1, Specialist Periodical Reports, The Chemical Society, Burlington House, London, 1970, p 135; also Vol. 2, 1972, pp 8–10.

(4) L. Eberson, *J. Amer. Chem. Soc.*, **89**, 4669 (1967).

(5) R. A. Firestone, D. F. Reinhold, W. A. Gaines, J. M. Chemerda, and M. Sletzinger, *J. Org. Chem.*, **33**, 1213 (1968).

(6) The experimental evidence does not rule out formation of **6** and **7** by nucleophilic attack of acetate on **4** and **3**, respectively. This seems quite unlikely, however. If **6** and **7** formed by oxazoline ring opening,[7] one would expect their ratios to be reversed on two counts: first, there is more **3** to start with; and second, the transition state for **4** to **6** suggests greater nonbonded interaction (aryl–methyl) than **3** to **7** (aryl–nitrile).

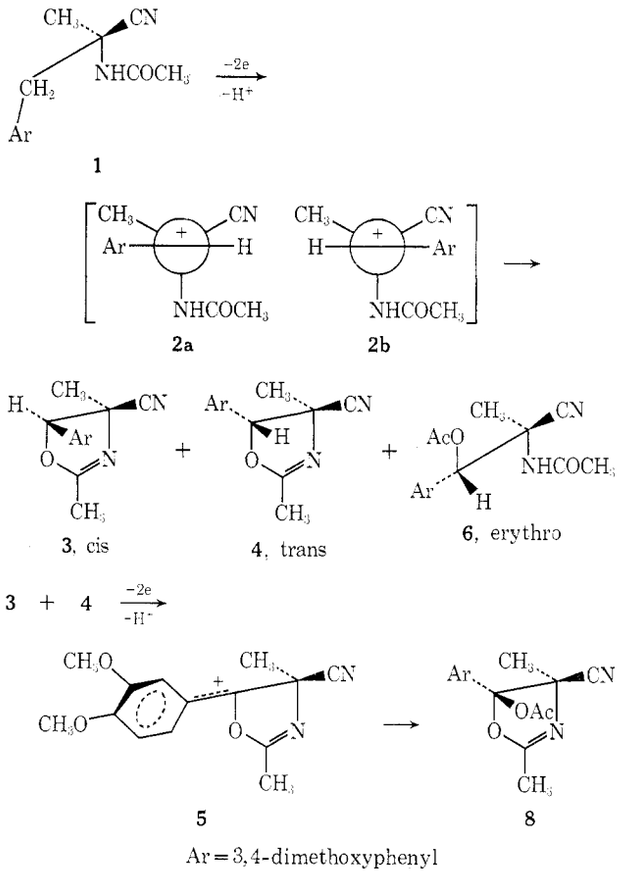
(7) S. H. Pines, M. A. Kozlowski, and S. Karady, *J. Org. Chem.*, **34**, 1621 (1969).

(8) The formation of aldehydes at the anode has frequently been attributed to traces of water and/or overoxidation. Here, formation of **9** requires cleavage of a C–C bond. A recent paper[9] describes conditions for preparation of aldehydes from $ArCH_2X$ compounds in good yields; however, ketones were formed from ArCHXR starting materials.

(9) E. A. Mayeda, L. L. Miller, and J. F. Wolf, *J. Amer. Chem. Soc.*, **94**, 6812 (1972).

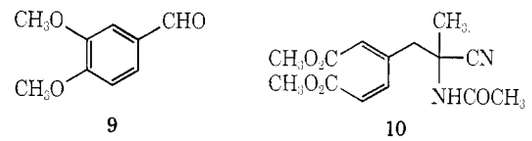
CHART I

ANODIC OXIDATION OF 1



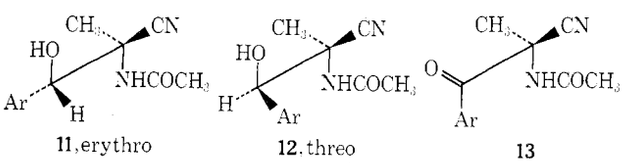
Ar = 3,4-dimethoxyphenyl

sible to isolate traces of (*S*)-3-[3-(2-cyano-2-acetamido)-propyl]-*cis*,*cis*-2,4-hexadienedioic acid dimethyl ester (**10**). The latter results from oxidative cleavage of the



veratryl moiety, a type reaction which has both conventional reagent[10] and electrochemical[11] precedent.

The configurations of **3**, **4**, and **8** were assigned mainly by nmr. With similar isomeric oxazolines, it has been established that the isomer with both the aryl and methyl groups on the same side possesses the distinctly higher field 4-methyl signal.[12] Since **3** and **6** gave, upon aqueous hydrolysis, the same (2*R*,3*S*)-2-acetamido-3-(3,4-dimethoxyphenyl)-3-hydroxy-2-methylpropionitrile (**11**), the erythro configuration of **6** is assured. Hydrolysis of the mixture of **4** and **8** gave threo isomer **12** and keto nitrile **13**, thus confirming both



(10) R. B. Woodward, M. P. Cava, W. D. Ollis, A. Hunger, H. U. Daeniker, and K. Schenker, *Tetrahedron*, **19**, 247 (1963).

(11) B. Belleau and N. L. Weinberg, *J. Amer. Chem. Soc.*, **85**, 2525 (1963).

(12) S. H. Pines, S. Karady, M. A. Kozlowski, and M. Sletzinger, *J. Org. Chem.*, **38**, 1762 (1968).

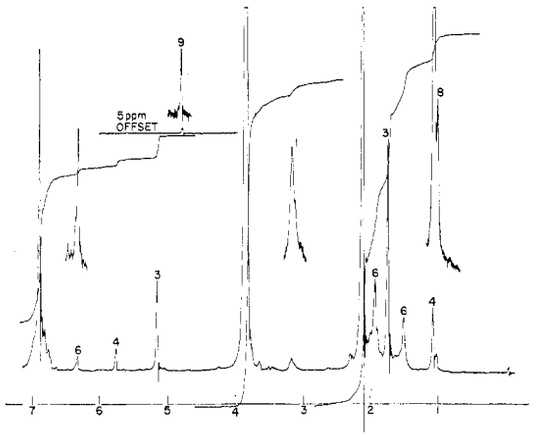
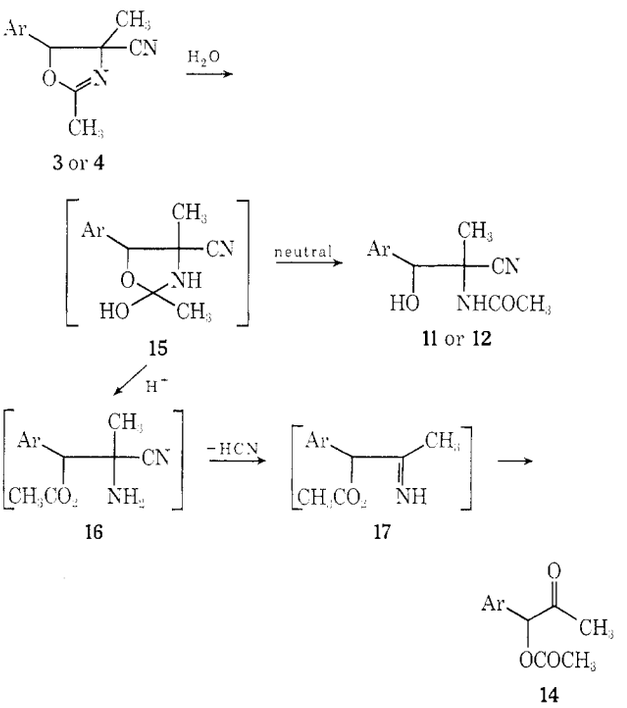


Figure 1.—60-MHz nmr spectrum of the total organic product of electrolysis. The numbers at several of the signals refer to the structures to which those signals have been assigned.

the structures of **4** and **8**, and the stereochemistry of **4**. The structure **13** emphasizes again that **8** is a product of two oxidation stages.

A trivial product, 1-acetoxy-1-(3,4-dimethoxyphenyl)-2-propanone (**14**),[13] was found in some chromatography fractions but was not observed by gas chromatography–mass spectral analysis of the electrolysis reaction *per se*. If hydrolysis of an oxazoline occurred on an adsorbent such as silica, loss of HCN and hydrolysis of the resulting imine, **17**, would lead to formation of **14** (Chart II).

CHART II



Reaction of **1** with manganic acetate in acetic acid–acetic anhydride gave the same oxazolines **3** and **4** in nearly the same ratio, approximately 3:1. This reaction has been cited previously as being mechanistically

(13) **14** was previously reported [H. L. Slates, D. Taub, C. H. Kuo, and N. L. Wendler, *J. Org. Chem.*, **29**, 1424 (1964)] from $Pb(OAc)_4$ oxidation of optically active *N*-acetyl-α-methyl-3,4-dimethoxyphenylalanine without rotational data. In the present instance, **14** is optically active.

similar to anodic acetoxylation.[4,14,15] The overall yield was much lower with $Mn(OAc)_3$, attesting to the advantages of the electrochemical method for synthesis.

Of more significance, the product ratio from the homogeneous reaction, paralleling the ratios obtained *via* electrolysis, discounts any striking steric effect attributable to reaction *at* the anode. One must conclude, therefore, that in the electrolysis either adsorption of the conformers of **2** is not widely disparate, or the product-forming final step occurs after desorption of **2** from the electrode.

Having established that a stereochemical bias does exist in the anodic reaction but that it is not appreciably different from the stereoselectivity of an analogous homogeneous reaction, it is worthwhile asking whether the bias is predictable. If the intermediacy of a benzylic cation can be accepted for both reactions,[1,2,4,14,15] then this cation can be represented by (at least) the two conformers of **2** shown in Chart I. Cyclization of **2b** should be favored over **2a**, since, at the point of bond formation, there is less nonbonded interaction in **2b** (Ar to CN) than **2a** (Ar to CH_3).

In the light of these results, and Eberson's recent stereochemical study with 2-*tert*-butylindan,[16] where he concludes with "... several reasons why 2-*tert*-butylindane is not an ideal model system for stereochemical study ...," it is interesting to speculate on what kind of substrate would provide "drastic differences in the cis–trans ratio between the electrochemical and homogeneous reactions ...."[16] In addition to the steric limitations he discusses, perhaps there should be added an electronic limitation. Thus, a "too stable cation" might be too readily desorbed from the anode prior to conversion to product. A "too unstable cation," on the other hand, might require higher electrode potentials for its formation, thereby diminishing the possibilities of reaction selectivity, a great promise of organic electrochemistry.

Experimental Section[17]

Cell Assembly.—The electrolyses were performed in a covered, water-jacketed cell of 250-ml capacity. A dry nitrogen atmosphere was maintained throughout. Unless otherwise specified, the anode consisted of a cylinder of platinum mesh, 2-in. diameter, 2.25 in. high. The cathode was 1 in. × 1 in. platinum foil separated from the anode compartment by a medium-porosity glass frit. Mixing was by a Teflon-covered magnetic stirring bar. A Wenking Model 70HV 1/90 potentiostat was used in conjunction with a saturated calomel electrode to control the potential.

Analytical Procedures.—Aliquots of the electrolysis were transferred by syringe into dry flasks and pumped to dryness without applied heat. The residue was taken up in sieve-dried ethyl acetate, separated from the crystalline sodium acetate, and evaporated as before, and the process was repeated with dry benzene. Vapor phase and thin layer chromatography were performed with dry solvents and protection from moisture; nmr spectra were usually run in $CDCl_3$. The vpc column which was used (3% OV-1 on Supelcoport, 5 ft × 0.25 in.) did not permit separation of the isomeric oxazolines **3** and **4**. The tlc systems, $CHCl_3$ with 0.5–4% MeOH, or benzene with 1–3% acetone, did not separate (4*R*,5*R*)-oxazoline **4** from acetoxy oxazoline **8**. All other compounds were resolved; some separations required multiple development.

Electrolysis.—The electrolyte was made by warming 200 ml of glacial acetic acid, 12.5 ml of acetic anhydride, and 12 g of anhydrous sodium acetate for 1 hr at 80–90°. To 200 ml of this cooled solution was added 6 g of **1**, and the stirred solution was electrolyzed at 1.14 V (*vs.* sce) and 18–20° with an initial-current of 18 mA. The reaction was continued until the current dropped to 5 mA. Solvent and sodium acetate were removed as described for the aliquots.

Isolation and Characterization of the Products.—A 0.5-g portion of the above residue was separated by chromatography on three 2-mm, 20 × 20 (E. Merck) preparative plates with 4% MeOH in $CHCl_3$. Column chromatography (Baker silica gel) was aggravated by continuing hydrolysis throughout (see section on hydrolysis). Seven bands, A to G, were obtained. The products in each are discussed below, in order of increasing polarity.

Band A weighed 17 mg. The major constituent was 3,4-dimethoxybenzaldehyde (**9**), identical with (ir, nmr) and inseparable from (tlc, vpc) an authentic sample. A tlc eluate of a second, lesser spot showed significant fragments at *m/e* 209, 167, and 139, suggesting partial structure $(CH_3O)_2C_6H_3CH(OCOCH_3)$–. It was not further characterized.

Band B weighed 84 mg. This fraction was a mixture of the (4*R*,5*R*)-oxazoline **4** and acetoxy oxazoline **8** in a ratio of *ca.* 2.5–3 to 1: nmr ($CDCl_3$) δ 6.65–7 (m, 3, aromatic), 5.75 (s, 0.75, CH), 3.9 (s, 6, OCH_3), 2.2, 2.15 (s, 4$^+$, CH_3C=), 1.1, 1.07 (s, 3$^-$, CH_3C<); gc–mass spectrum *m/e* (rel intensity) peak 1 (**4**) 260 (M^+, 50), 233 (<0.5), 218 (29), 167 (13), 139 (5), 94 (100); peak 2 (**8**) 318 (M^+, 3), 259 (3), 190 (6), 165 (100), 94 (>100); ir ($CHCl_3$) 1785 (ester C=O) and 1665 cm^{-1} (C=N). The two products were not further separated.

Band C weighed 205 mg. This fraction deposited 187 mg of crystalline (4*R*,5*S*)-oxazoline **3** from 1:1 ether–hexane, mp 84–87°. Recrystallization from ether–hexane after filtration in benzene gave an analytical sample: mp 87.5–89°; nmr ($CDCl_3$) δ 6.87 (m, 3, aromatic), 5.1 (s, 1, CH), 3.93, 3.91 (each) (s, 3, OCH_3), 2.15 (s, 3, CH_3C=), 1.77 (S, 3, CH_3C<); mass spectrum very similar to that of **4** (above); ir (Nujol) 1670 cm^{-1} (C=N); $[\alpha]D$ +90° (*c* 4, $CHCl_3$).

Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.58; H, 6.25; N 10.44.

Band D weighed 15 mg and contained mainly the (4*R*,5*S*)-oxazoline **3** and its hydrolysis product **11**, which is characterized below.

Band E weighed 146 mg. The benzylic proton at δ 6.2 could be equated with 65% of the total methoxy signal. The starting material, **1**, was also present. Rechromatography on three 1-mm 20 × 20 (Analtech Labs) plates with 3X development, 4% MeOH in $CHCl_3$, gave a fraction which yielded 30 mg of crystalline **6**: mp 171–172.5° from ethyl acetate–hexane; nmr ($CDCl_3$) δ 6.9 (m, 3, aromatic), 6.15 (s, 1, CH), 6.25 (broad s, 1 NH), 3.86 (s, 6, OCH_3), 2.2 (s, 3, CH_3C=), 1.98 (s, 3, CH_3C=), 1.55 (s, 3, CH_3–C<); mass spectrum 320 (M^+, 0.5), 261 (1), 219 (2.5), 209 (12), 167 (100), 139 (28), 112 (13); as its TMS derivative, 392 (M^+), 167 (100); ir (Nujol) 3280 (NH), 1760 (ester C=O), 1660 cm^{-1} (amide C=O).

Anal. Calcd for $C_{16}H_{20}N_2O_5$: C, 59.99; H, 6.29; N, 8.75. Found: C, 60.17; H, 6.47; N, 8.66.

Band F weighed 21 mg. The nmr spectrum was interpretable most readily as that of a pair of isomeric compounds. Since half of the singlets corresponded to **6**, the presence of the isomer **7** was inferred from the others.

6, δ	Assignment	**7**, δ
6.15	CH	6.23
2.16	CH_3C=	2.13
1.97	CH_3C=	1.9
1.5	CH_3C<	1.68

The two isomers were separated by gc and the individual eluates gave almost identical mass spectra (M^+ 320, remainder of spec-

(14) P. J. Andrulis, Jr., M. J. S. Dewar, R. Dietz, and R. L. Hunt, *J. Amer. Chem. Soc.*, **88**, 5473 (1966), and succeeding papers in the series.

(15) J. P. Dirlam and L. Eberson, *Acta Chem. Scand.*, **26**, 1454 (1972).

(16) L. Eberson and H. Sternerup, *Acta Chem. Scand.*, **26**, 1431 (1972). This paper, and its companion, ref 15, appeared in print after the completion of the above work. In it, the authors clearly and succinctly trace the background of the stereochemistry *vs.* adsorption postulate.

(17) Melting points are uncorrected. Elemental analyses were performed by Mr. R. N. Boos and his associates of these laboratories. Ir spectra were usually obtained on a Perkin-Elmer 137. Nmr spectra were obtained with a Varian A-60A or Jeolco C-60HL spectrometer. Mass spectra were obtained with an LKB-9000 spectrometer at 70 eV. For brevity, only portions of some spectra are reported. Commerical tlc and preparative silica plates from Analtech Labs, E. Merck, and Quantum Industries were used.

trum as described above for 6). The TMS derivatives were also separable and gave the proper mass spectra. Preparative separation was not attempted.

Band G weighed 22 mg. The major constituent was the *erythro*-hydroxyamidonitrile **11** (nmr, tlc). Its characterization is described directly below.

Hydrolysis of the Oxazoline 3.—Several milligrams of **3** was left at room temperature overnight in 90% acetic acid. The residue was essentially a single component (tlc, 4% MeOH in $CHCl_3$) of greater polarity than **3**. Crystallization from ethyl acetate–ether and then from ethyl acetate gave pure **11**: mp 127–132°;[18] nmr ($CDCl_3$) δ 6.8–7.1 (m, 3, aromatic), 6.65 (broad s, 1, NH), 4.9 (d, 1, J = 4 Hz, CH), 4.5 (d, 1, J = 4 Hz, OH), 3.85 (s, 6, OCH_3), 2.0 (s, 3, $CH_3C{=}$), 1.45 (s, 3, $CH_3C{<}$); mass spectrum 278 (M^+, <0.01), 203 (1), 167 (100), 139 (70), 112 (2.5); as the bis TMS derivative, 407 (M^+ − 15), 239 (100); ir (Nujol) 3550, 3500, 3300, 3250 (NH, OH), 2250 (C≡N), 1650 cm^{-1} (amide C=O); $[\alpha]D$ −54.4° (*c* 6, CH_3OH).

Anal. Calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.38; H, 6.55; N 10.03.

Hydrolysis of the Oxazoline 4 and the Acetoxy Oxazoline 8 Mixture.—Most of the band B mixture was hydrolyzed in 90% acetic acid as with **3**. The residue was chromatographed twice with 4% MeOH in $CHCl_3$ on a 2-mm 20 × 20 (Analtech) preparative plate. Two products were isolated. The first was (*R*)-2-acetamido-2-(3,4-dimethoxybenzoyl)propionitrile (**13**) (17 mg) as crystals from MeOH: mp 163.5–164.5°; nmr ($CDCl_3$) δ 8 (q, 1, J = 9 Hz, aromatic C_6H), 6.65 (d, 1, J = 2 Hz, aromatic C_2H), 6.93 (d, 1, J = 9 Hz, aromatic C_5H), 7.37 (broad s, 1 NH), 3.93, 3.99 (each) (s, 3, OCH_3), 2.06, 2.11 (each) (s, 3, CH_3); mass spectrum *m/e* 276 (M^+, 2), 165 (100), 137 (12), 122 (5); ir (Nujol) 3290, 3250, 3200 (NH), 2250 (C≡N), 1690 (C=O), 1650 cm^{-1} (amide C=O). A second compound was (2*R*,3*R*)-2-acetamido-3-(3,4-dimethoxyphenyl)-3-hydroxy-2-methylpropionitrile (**12**), mp 115–118°[19] (ethyl acetate–ether). On tlc, **12** was separated with difficulty (slower) from **11**: nmr ($CDCl_3$) δ 6.7–7.1 (m, 3, aromatic), 6.35 (broad s, 1, NH), 5.05 (s, 1, CH), 3.85 (s, 6, OCH_3), 1.99 (s, 3, $CH_3C{=}$), 1.55 (s, 1, $CH_3C{<}$) [the OH signal was not observed until exchange with CD_3OD, whereupon the CD_3OH (δ 3.18) signal integrated for 2 H]; mass spectrum *m/e* 278 (M^+, <1), 260 (1), 219 (2.5), 210 (1.5), 167 (100), 139 (65), 112 (30). The mono TMS derivative had *m/e* 350 (M^+), 335, 239 (100); the bis TMS derivative had *m/e* 407 (M^+ − 15), 239 (100).

Hydrolysis of 6.—A solution of 2 mg of **6** in 0.2 ml of 85% MeOH–15% saturated sodium bicarbonate was left overnight. Tlc of the organic portion of the residue (4% MeOH in $CHCl_3$) alone and in admixture with **11** showed the hydrolysis product to be *erythro*-hydroxylamidonitrile, **11**. The threo isomer, **12**, was not detected.

Manganic Acetate Oxidation of 1 to Give 3 and 4.—A slurry of 1 g of $Mn(OAc)_3 \cdot 2H_2O$[20] in 10 ml of acetic acid and 3 ml of acetic anhydride was warmed at 70° for 2 hr with stirring. To it was added 200 mg of **1** and the reaction mixture was stirred at 65° overnight under N_2. The solvent was removed *in vacuo* below 45°, and the residue was dissolved in $CHCl_3$ and filtered to remove inorganics. Final traces of Mn salts were removed by passage through a small bed of silica, followed by ethyl acetate. The nmr spectrum of the residue (~150 mg) showed the presence of about 40% **1** and 20–25% of **9**. Both oxazolines, **3** and **4**, were present.

Separation on a 2-mm 20 × 20 (E. Merck) preparative plate with 2% MeOH in $CHCl_3$ gave about 20 mg of the mixed oxazolines, **3** and **4**, clearly identifiable by nmr, tlc, and mass spectrum.

(*S*)-3-[3-(2-Cyano-2-acetamido)propyl]-*cis*,*cis*-2,4-hexadienedioic Acid Dimethyl Ester (10).—Electrolysis of 750 mg of **1** in 150 ml of 0.35 *M* NaOAc–HOAc at 1.7 V in an uncooled, undivided cell overnight gave a gross mixture (tlc). Preparative plate (E. Merck) chromatography (3% MeOH in $CHCl_3$) gave the aldehyde **9** and a crystalline material, uv λ_{max} 210 mm, λ_{infl} ~250 nm, with an R_f just slightly less than that of **1**. The analytical sample, mp 153–156° (ethyl acetate), was shown to be **10**: nmr ($CDCl_3$) δ 7.1 (d of d, 1, J = 12.5 Hz, C_4 H), 6.03 (m, 2, C_2 and C_4 H's), 6.6 (broad s, 1, NH), 3.66, 3.7 (each) (s, 3, OCH_3), 3.05 (q, 2, CH_2), 2.0 (s, 3, $CH_3C{=}$), 1.75 (s, 3, $CH_3C{<}$); mass spectrum *m/e* 294 (M^+, 0.5), 263 (1.5), 252 (5), 235 (35), 221 (18), 194 (22), 183 (90), 176 (100), 152 (53), 124 (70); the TMS derivative had *m/e* 366 (M^+); ir (Nujol) 3320 (NH), 1735 (ester C=O), 1665 cm^{-1} (amide C=O).

Anal. Calcd for $C_{14}H_{18}N_2O_5$: C, 57.13; H, 6.17; N, 9.52. Found: C, 56.81; H, 6.03; N, 9.44.

The same compound was observed (nmr, tlc) in trace quantities from a "usual" electrolysis of **1** in a divided cell at 1.14 V.

Isolation of 1-Acetoxy-1-(3,4-dimethoxyphenyl)-2-propanone (14).—When the least polar fractions from a silica gel column chromatograph were examined by tlc (2.5% acetone in benzene, then 2% MeOH in $CHCl_3$), a new component was observed with an R_f between that of **9** and the **4**–**8** mixture. It was first separated by 3X development on E. Merck tlc plates, 250 μ, with 5% acetone in benzene, and shown to be **14**, an oil: nmr ($CDCl_3$) δ 6.7–7 (m, 3, aromatic), 5.9, (s, 1, CH), 3.85 (s, 6, OCH_3), 2.1, 2.17 (each) (s, 3, $CH_3C{=}O$); ir (neat film) 1735, 1750 cm^{-1}; mass spectrum *m/e* 252 (M^+, 15), 209 (47), 167 (100), 139 (78); ORD (MeOH) (λ, [α], description) 305, −4900, − trough; 292, 0, cross; 278, +5710, + peak; 267, +5450, + trough; 258, +5950, + peak.

Acknowledgment.—Thanks are due to Mr. Jack Smith for mass spectra and assistance in their interpretation and to Mr. R. C. Zerfing and Mrs. E. Maitheny for nmr and ORD spectra. I wish particularly to acknowledge stimulating and helpful discussions with Dr. A. W. Douglas.

Registry No.—**1**, 38188-53-3; **3**, 41674-68-4; **4**, 41674-69-5; **6**, 41674-70-8; **7**, 41674-71-9; **8**, 41674-72-0; **10**, 41755-30-0; **11**, 41674-73-1; **12**, 41674-74-2; **13**, 41674-75-3; **14**, 38007-20-4.

(18) Other samples showed a variety of melting points: 121–126°, 168–170°, etc., suggesting polymorphism.

(19) On a hot stage. Dta: endotherm at 128°.

(20) Made by the method of footnote 4, J. B. Bush, Jr., and H. Finkbeiner, *J. Amer. Chem. Soc.*, **90**, 5903 (1968).