The Anodic Oxidation of *cis*-1,2,3,4-Tetrahydronaphthalene-2,3-dicarboxylic Acid and Its Derivatives: Competition between Oxidative Bisdecarboxylation and Dilactone Formation

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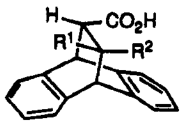
Received January 20, 1993

Introduction

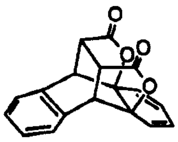
The low reactivity, hazardous nature, and inconvenience of acetylene as a dienophile in the Diels–Alder reaction have led to the development of synthetically equivalent dienophiles, e.g. *p*-tolyl ethynyl sulfone,[1] adducts of which may be reduced to give compounds that are formally Diels–Alder adducts of acetylene. Maleic anhydride reacts readily with a wide range of dienes to give Diels–Alder adducts, which are often easily convertible into the corresponding acetylene adducts by hydrolysis followed by oxidative bisdecarboxylation. This oxidation may be accomplished anodically[2] or by reagents such as lead(IV) acetate[3] or copper(I) oxide.[4] The electrochemical approach is usually high yielding, but there have been reports of side reactions attributable to rearrangements of an intermediate carbenium ion formed after the first decarboxylation step. Here we report that electrochemical oxidation of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,-12-dicarboxylic acid (**1a**) gave the unexpected hexacyclic dilactone **2** (42% yield) by a novel reaction involving the intramolecular 1,2-addition of the carboxy groups to an aryl residue. The scope and possible mechanism of this reaction are discussed. A convenient cathodic method for formation of the dicarboxylic acids is also described; it involves electrogeneration of *o*-quinodimethanes with *in situ* Diels–Alder trapping.

Results and Discussion

The dicarboxylic acid **1a** was electrolyzed in pyridine–water (9:1) in the presence of triethylamine, using a pair of closely spaced (5 mm) parallel platinum plates (25 × 25 mm) and an initial current density of 39 mA cm^{-2}; these conditions are similar to those previously used to effect oxidative bisdecarboxylation. After the passage of 2.4 fmol^{-1} with respect to the diacid **1a**, the expected bisdecarboxylation product 9,10-dihydro-9,10-ethenoanthracene (**3a**) could be isolated in only 10% yield, whereas a 42% yield of the crystalline dilactone **2** was obtained. The structure of dilactone **2** was suggested by IR spectroscopy (ν_{max} 1793 cm^{-1}, γ-lactone C=O) and ^{1}H NMR spectroscopy (including an AA′BB′ system in the olefinic region) and was confirmed by a single crystal X-ray structure determination.[5]



1a $R^1 = H; R^2 = CO_2H$
1b $R^1 = CO_2H; R^2 = H$



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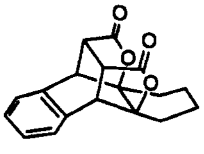
3a $X = o\text{-}C_6H_4$
3b $X = [CH_2]_2$

The dilactone **2** is a rigid molecule containing a variety of reactive sites and so has possible applications in the construction of host molecules for use as synthetic receptors. The use of the 1,3-diene moiety in addition reactions was illustrated by selective hydrogenation to give the dilactone **4** and by a Diels–Alder reaction with 4-phenyl-1,2,4-triazoline-3,5-dione to yield the cycloadduct **5**, which was shown by X-ray crystallography[5] to have arisen by attack of the dienophile on the face of the diene which was *syn* to the acyloxy groups.



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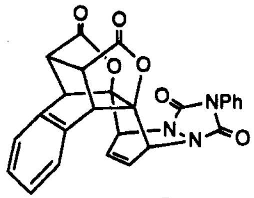

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In order to define the scope of the lactonization reaction, we investigated the effects of varying the method of oxidation, the stereochemical relationship between the carboxyl groups, the nature of the bridge linking the 1- and 4-positions of the 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic acid derivative and the susceptibility of the aryl group towards single-electron oxidation.

Method of Oxidation. The dicarboxylic acid **1a** has been reported to undergo cycloreversion to anthracene upon attempted oxidation by CuO in hot quinoline.[4] The oxidation of the diacid **1a** by $Pb(OAc)_4$ in benzene–pyridine has been claimed[6] to give the hydrocarbon **3**, but no data were given to support the structure of this product. We confirmed that under the latter conditions the product is indeed the hydrocarbon **3a**, which was identified by ^{1}H NMR and mass spectrometry and which had an identical mp to material prepared by an alternative route.[7] There was no evidence for the formation of the dilactone **2** when $Pb(OAc)_4$ was the oxidant; thus lactonization appears to be unique to the electrochemical method of oxidation.

Stereochemical Relationship between the Carboxyl Groups. Attempted electrochemical oxidation of *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (**1b**) under identical conditions to those used for the *cis*-diacid **1a** failed to give either the dilactone **2** or the hydrocarbon **3a**. Instead the starting diacid **1b** was recovered (31%).

Nature of the Bridging Group. (1*R**,2*S**,3*R**,4*S**)-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-dicarboxylic acid (**6a**) is an analogue of the diacid **1a** in which an ethylene bridge replaces the *o*-phenylene group. The

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[2] Utley, J. H. P. In *Technique of Electroorganic Synthesis*; Weinberg, N. L. Ed., John Wiley and Sons Inc.: New York, 1974.

[3] Grob, C. A.; Ohta, M.; Renk, E.; Weiss, A. *Helv. Chim. Acta*, 1958, *41*, 1191–1197.

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[5] The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ U.K.

[6] Grob, C. A.; Ohta, M.; Weiss, A. *Angew. Chem.*, 1958, *70*, 343–344.

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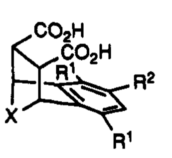
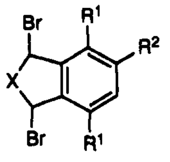
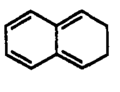
corresponding anhydride **9a** has previously been prepared in 46% yield by the Diels–Alder reaction between maleic anhydride and transient 2,3-dihydronaphthalene (**8**) (formed from the reduction of 1,4-dibromo-1,2,3,4-tetrahydronaphthalene (**7a**) with finely divided nickel).[8]



6a $X = [CH_2]_2$; $R^1 = R^2 = H$
6b $X = 2 \times H$; $R^1 = R^2 = H$
6c $X = 2 \times H$; $R^1 = OMe$; $R^2 = H$
6d $X = [CH_2]_2$; $R^1 = H$; $R^2 = OMe$



7a $X = [CH_2]_2$; $R^1 = R^2 = H$
7b $X = 2 \times H$; $R^1 = R^2 = H$
7c $X = 2 \times H$; $R^1 = OMe$; $R^2 = H$
7d $X = [CH_2]_2$; $R^1 = H$; $R^2 = OMe$



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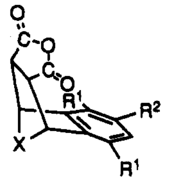
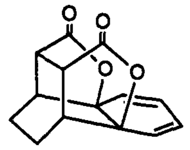


9a $X = [CH_2]_2$; $R^1 = R^2 = H$
9b $X = 2 \times H$; $R^1 = R^2 = H$
9c $X = 2 \times H$; $R^1 = OMe$; $R^2 = H$



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In an alternative approach we used cathodic reduction of 1,4-dibromo-1,2,3,4-tetrahydronaphthalene (**7a**) to generate 2,3-dihydronaphthalene (**8**), which underwent an *in situ* Diels–Alder reaction with maleic anhydride. By the electrochemical method [−1.4 V (Ag/AgBr); Hg pool cathode; 0.1 M Et_4NBr in DMF; divided cell] a higher yield (58%) of the anhydride **9a** was obtained. The anhydrides **9b** (44% yield) and **9c** (31% yield) were prepared similarly from the appropriate dibromides **7b** and **7c**. All three anhydrides were hydrolyzed by sodium hydroxide in aqueous tetrahydrofuran to give the corresponding dicarboxylic acids **6a–6c** in excellent yields (>92%).

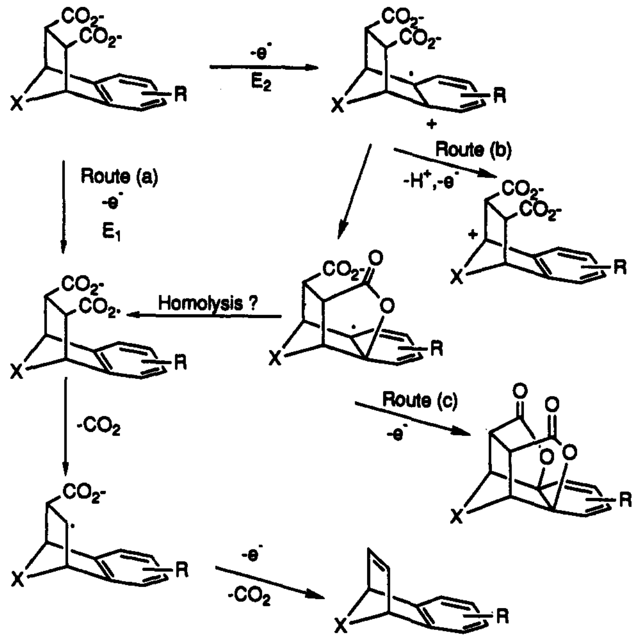
Electrochemical oxidation of the diacid **6a** using the conditions specified above gave the dilactone **10** in 10% yield, together with a 4% yield of 1,4-dihydro-1,4-ethanonaphthalene (**3b**).

cis-1,2,3,4-Tetrahydronaphthalene-2,3-dicarboxylic acid (**6b**) is an analogue of the diacid **1a** which lacks the *o*-phenylene bridge. Electrochemical oxidation of the diacid **6b** did not lead to dilactone formation, but occurred predominantly through oxidative bisdecarboxylation to give 1,4-dihydronaphthalene, which was largely converted into naphthalene under the conditions of the electrolysis. The crude product was dehydrogenated to pure naphthalene (72% yield) by refluxing in ethyl acetate with 5% palladium-on-carbon for 1 h.

Mechanistic Rationalization. The key factors which need to be reconciled in a mechanistic hypothesis are (i) the retention of the carboxylate groups; (ii) the necessity for the carboxylate groups to project over the aromatic ring; (iii) the apparent requirement, for dilactone formation, of a benzobicycloalkane unit.

We propose the mechanism outlined in Scheme I. Oxidation of the dicarboxylate is at controlled current and at relatively high current density. Under these conditions the anode potential will be high; usually this results in carboxylate oxidation with subsequent decarboxylation [route a]. Alternatively the aromatic ring might be oxidized. For benzylic systems this could result in proton loss and further oxidation to a benzylic cation [route b].[9] However, for the bicycloalkane systems this would result in the formation of a nonplanar benzylic cation, known to be energetically disfavored. In these special circumstances, and with the carboxylate functions suitably oriented, dilactone formation becomes preferred [route c].

Scheme I



Ease of Oxidation of the Aromatic Ring. A possible test for the prior oxidation of the aromatic ring is to determine the effect of ring substitution on product formation and ease of oxidation. Consequently we examined the anodic oxidation of substrates containing one or more methoxyl substituents in the aromatic ring. In the case of the diacid **6c** there was no evidence for the formation of any corresponding dilactone and there was extensive production of tarry, presumably polymeric material, consistent with the predominance of route b in Scheme I. We therefore attempted to construct the bridged system **6d**, but unfortunately we were unable to prepare the required dibromide **7d**, which appeared to be very susceptible to aromatization.

Cyclic Voltammetric Experiments. The oxidative behavior of four of the dicarboxylic acids at a platinum bead anode and in acetonitrile solution was examined by cyclic voltammetry. The results are summarized in Table I.

In each case irreversible oxidation was observed, implying rapid followup reactions after the initial electron transfer. Compound **1a**, which on anodic oxidation gave the dilactone **2**, was oxidized at a significantly less positive potential (relative to Ag/Ag^+) than the related compound **6a**. The second benzene ring is therefore not only associated with more efficient bislactonization, but also

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Table I. Oxidation Peak Potentials[a]

compound	1a	6a	6b	6c
$E_{p,a}$ (V vs Ag/Ag$^+$)	1.81	2.34	1.55	0.98

[a] Pt bead anode; CH_3CN–Bu_4NBF_4 (0.1 M); sweep speed 0.45 V s^{-1}. All peaks were irreversible, and for compounds **1a** and **6a** appeared as shoulders on the background oxidation current.

with easier oxidation. The difference in oxidation peak potentials [$E_{p,a}$(**6a**) – $E_{p,a}$(**1a**) = 0.53 V] is substantial and probably reflects a difference in the standard oxidation potentials ($E°$), although peak potentials are also a function of the rates of followup reactions.[10] Consequently a less positive value for **1a** than for **6a** would result from a faster followup reaction, such as bislactonization, after the initial oxidation. Alternatively, if it could be established that the difference was in the $E°$ values, an explanation would need to be in terms of special factors influencing the ionization potential of **1a** *vis à vis* **6a**. The absence of a bridging ethylene group, as in **6b**, allows easier oxidation compared with **6a**. It is not obvious why such a large shift in this case should reflect a big difference in $E°$ values. However, in **6a** the bridged structure would preclude rapid proton loss leading with further oxidation to a bridgehead cation. Also, the bridgehead C–H bonds would be stereoelectronically incapable of stabilizing a neighboring radical-cation by hyperconjugation. Both factors would argue for easier oxidation of **6b** compared with **6a**. The oxidation peak potential of **6c** is much less positive than for **6b**, confirming the expectation that substitution of the aryl residue by methoxyl groups should aid its oxidation.

In summary, electrochemical oxidation of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (**1a**) gives the novel hexacyclic dilactone **2**. The electrochemical reduction of 1,2-bis(bromoalkyl)arenes **7a–c** is an efficient method for generating *o*-quinodimethane derivatives, which with maleic anhydride give substituted 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydrides **9a–c**. However, hydrolysis and oxidation of these anhydrides gives poor or no yields of dilactones analogous to **2**, since other oxidation routes, including decarboxylation and benzylic oxidation, are preferred.

Experimental Section

General Procedures. Organic extracts were dried over $MgSO_4$ and evaporated under reduced pressure. "Petrol" refers to the light petroleum ether fraction of bp 40–60 °C.

Electrochemical Oxidation of *cis*-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (1a). A solution of **1a** (0.25 g, 0.85 mmol) in 9:1 pyridine–water (20 cm^3) containing Et_3N (0.12 cm^3, 0.86 mmol) was placed in a water-cooled, undivided cell containing two platinum foil electrodes (25 × 25 mm) set 5 mm apart. The mixture was stirred and flushed with nitrogen for 10 min and amperostatic electrolysis carried out. The current was 245 mA (39 mA cm^{-2}); in this particular cell the voltage was ca. 85 V. During the electrolysis the polarity of the electrodes was occasionally reversed to remove fouling. After the passage of 2.4 fmol^{-1} with respect to **1a**, the current had decreased to 52 mA and the cell voltage had increased to the maximum deliverable by the power supply (110 V). The cell contents were poured onto ice (15 g) and acidified with concd H_2SO_4. The mixture was then extracted with CH_2Cl_2 (4 × 5 cm^3), and the combined organic extracts were washed with aqueous $NaHCO_3$ (2 × 5 cm^3) and water (5 cm^3) and then dried ($MgSO_4$). Evaporation of the CH_2Cl_2 followed by recrystallization from toluene gave the dilactone **2** (0.105 g, 42%) as colorless needles: mp 284–285 °C; IR (KBr) 1793 cm^{-1}; ^1H NMR (250 MHz, DMSO-d_6) 3.15 (t, J = 2 Hz, 2 H), 5.72–5.80 (m, 2 H), 5.87–5.95 (m, 2 H), 7.38 (s, 4 H); ^{13}C NMR (63 MHz, DMSO-d_6) 43.9, 50.7, 81.2, 124.3, 126.3, 126.5, 128.3, 132.7, 174.9; mass spectrum, *m/e* (rel inten) 248 (16, M$^+$ – CO_2), 156 (33), 128 (100). Single crystals suitable for X-ray diffraction were prepared by slow evaporation of a solution of **2** in toluene and initially contained one molecule of toluene of crystallization. Since the crystals easily lost toluene by evaporation, the crystal used in the diffraction experiment was sealed in a tube containing toluene vapour. The mother liquor from the crystallization was concentrated and subjected to flash chromatography, eluting with CH_2Cl_2–petrol (1:1). The first-eluted product was **3a** (25 mg, 10%): mp 119 °C (lit.[7] 119–120.5 °C).

Hydrogenation of the Dilactone 2. A solution of **2** (70 mg, 0.239 mmol) in 1:1 EtOAc–AcOH (12 cm^3) was shaken with 5% Pd-on-C (30 mg) under H_2 (2 bar) at 20 °C for 48 h. The mixture was filtered, concentrated, and recrystallized from AcOH to give the hydrogenated dilactone **4** (26.5 mg, 38%) as fine white crystals: mp 330–332 °C; IR (KBr) 1794 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) 1.16–1.33 (m, 2 H), 1.42–1.60 (m, 2 H), 1.71–1.88 (m, 4 H), 2.93 (t, J = 2 Hz, 2 H), 3.72 (t, J = 2 Hz, 2 H), 7.33–7.46 (m, 4 H); mass spectrum, *m/e* (rel inten) 268 (27), 155 (230), 128 (100). Anal. Calcd for $C_{18}H_{16}O_4$: C, 73.0; H, 5.4. Found: C, 72.7; H, 5.5.

Reaction of the Dilactone 2 with 4-Phenyltriazoline-3,5-dione. A solution of 4-phenyl-1,2,4-triazoline-3,5-dione (37.5 mg, 0.214 mmol) in acetone (3 cm^3) was added dropwise to the dilactone **2** (52.2 mg, 0.179 mmol) in acetone (2 cm^3) at 20 °C. After 20 min, the white crystals of the adduct **5** (45.3 mg, 54%) were collected: mp > 300 °C; IR (KBr) 1799, 1775 and 1755 cm^{-1}; ^1H NMR (250 MHz, DMSO-d_6) 3.18 (t, J = 2 Hz, 2 H), 4.44 (s, 2 H), 5.41 (t, J = 4 Hz, 2 H), 5.74 (t, J = 4 Hz, 2 H), 7.30–7.54 (m, 9 H); mass spectrum, *m/e* (rel inten) 207 (24), 137 (68), 57 (100). Anal. Calcd for $C_{26}H_{17}N_3O_6$: C, 66.8; H, 3.7; N, 9.0. Found: C, 66.7; H, 3.5; N, 9.1.

(3a*R,4*S**,9*R**,9a*S**)-3a,4,9,9a-Tetrahydro-4,9-ethanonaphtho[2,3-*c*]furan-1,3-dione (9a).** The experiment was performed under N_2 in a cell divided by a polypropylene membrane, with a mercury pool working electrode, a carbon rod anode, and an Ag/AgBr reference electrode. 1,4-Dibromo-1,2,3,4-tetrahydronaphthalene[11] (**7a**) (2.00 g, 6.9 mmol) and maleic anhydride (1.36 g, 13.8 mmol) were coelectrolyzed at 20 °C in a 0.1 M solution of tetraethylammonium bromide in DMF (100 cm^3), using a reduction potential equal to the peak potential observed by cyclic voltammetry (–1.4 V against Ag/AgBr). The initial current was 400 mA. After 4.4 fmol^{-1} with respect to the dibromide **7a** had been passed, the mixture was partitioned between water (400 cm^3) and ether (2 × 100 cm^3). The combined ether extracts were combined and evaporated to give **9a** (0.92 g, 58%) as white crystals: mp 196–198 °C (lit.[8] 197–198 °C).

***cis*-3a,4,9,9a-Tetrahydronaphtho[2,3-*c*]furan-1,3-dione (9b).** This was prepared similarly to the anhydride **9a**, by coelectrolyzing 1,2-bis(bromomethyl)benzene (**7b**) (7.6 mmol) with maleic anhydride (22.8 mmol) in the presence of hydroquinone (0.4 mmol). The electrolysis was stopped when 2.6 fmol^{-1} with respect to the dibromide **7b** had been passed. Workup as before gave the anhydride **9b** (44%) as white plates, mp 187–190 °C (lit.[8] 184–185 °C).

***cis*-5,8-Dimethoxy-3a,4,9,9a-tetrahydronaphtho-[2,3-*c*]furan-1,3-dione (9c).** From **7c** (1.54 mmol) and maleic anhydride (7.71 mmol), by analogy with **9a** and **9b** above, using a reduction potential of –1.15 V (Ag/AgBr) and passing 2.4 fmol^{-1} with respect to the dibromide **7c**, the title anhydride **9c** (31% yield) was obtained as white crystals: mp 210–211 °C; IR (KBr) 1870 and 1800 cm^{-1}; ^1H NMR (80 MHz, DMSO-d_6) 2.80 (m, 4 H), 3.10 (m, 2 H), 3.80 (s, 6 H), 6.60 (s, 2 H); mass spectrum, *m/e* 262.0848, calcd for $C_{14}H_{14}O_5$ 262.0841; *m/e* (rel inten) 262 (100, M$^+$), 219 (15), 189 (31), 115 (22).

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(1*R,2*S**,3*R**,4*S**)-1,4-Ethano-1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic Acid (6a).** Hydrolysis of **9a** using NaOH (2.2 molar equiv in THF–H_2O) gave **6a** (98%) as a white solid, mp 199–200 °C (lit.[12] 195–197 °C).

Oxidation of (1*R,2*S**,3*R**,4*S**)-1,2,3,4-tetrahydro-1,4-ethanonaphthalene-2,3-dicarboxylic Acid (6a).** The diacid **6a** (0.116 g, 0.473 mmol) was oxidized electrochemically under identical conditions to those used for the diacid **1a**. Evaporation of the dichloromethane extract followed by recrystallization from toluene gave the dilactone **10** (11.2 mg, 10%) as colorless needles: mp 231–232 °C; IR 1799 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) 1.72–1.95 (m, 4 H), 2.45–2.49 (m, 2 H), 3.03 (t, $J = 2$ Hz, 2 H), 5.56–5.64 (m, 2 H), 6.20–6.27 (m, 2 H); mass spectrum m/z (rel inten) 246 (2, $M^+ + H_2$), 188 (12), 171 (39), 128 (100). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.8; H, 5.0. Found: C, 68.8; H, 5.1. The mother liquors were concentrated to give a brown oil (18 mg), which after flash chromatography in petrol gave 1,4-dihydro-1,4-ethanonaphthalene (**3b**) (5 mg, 4%) as a colorless oil. The ^1H NMR spectrum matched that reported in the literature.[13]

Acknowledgment. We thank the SERC and Merck Ltd. (B.D.H.) for a CASE award held by A.H.

Supplementary Material Available: ^1H NMR data for **9c** (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS; see any current masthead page for ordering information.

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