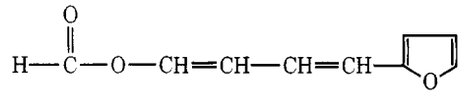
constitution of the formate of 1-hydroxy-4-(2-furyl)-1,3-butadiene (16) was deduced from the spectral and analytical



16

data. This is a new manner of oxetane ring cleavage in the 2,7-dioxabicyclo[3.2.0]hept-3-ene system.

Experimental Section

6-Carbobutoxy-2,7-dioxabicyclo[3.2.0]hept-3-ene (2). A solution of *n*-butyl glyoxylate (37.0 g) in furan (450 ml) was irradiated with a 400-W high-pressure mercury lamp under argon atmosphere in a Pyrex photochemical reactor. After 25 h the mixture was distilled and afforded 43.5 g (77.3%) of oxetane **2**: bp 86–88 °C (0.2 Torr); IR 1750, 1610 cm^{-1}; ^1H NMR (CCl_4) δ 6.59 (m, 1 H, $J_{1,3}$ = 1, $J_{3,4}$ = 2.3 Hz, H-3), 6.34 (d, 1 H, $J_{1,5}$ = 4.2 Hz, H-1), 5.34 (t, 1 H, $J_{4,5}$ = 2.8 Hz, H-4), 4.69 (d, 1 H, $J_{5,6}$ = 2.9 Hz, H-6). 3.69 (m, 1 H, H-5), signals of the *n*-butoxy group at 4.13 (t, 2 H) and 1.1–1.8 (m, 7 H). Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.6; H, 7.1. Found: C, 60.8; H, 7.1.

6-Acetoxymethyl-2,7-dioxabicyclo[3.2.0]hept-3-ene (3) was obtained from **2** by lithium aluminum hydride reduction followed by acetylation with acetic anhydride and pyridine in 53% overall yield: bp 83–86 °C (0.2 Torr); IR 1745, 1605 cm^{-1}; ^1H NMR (CCl_4) δ 6.65 (m, 1 H, $J_{3,4}$ = 3, $J_{3,5}$ = 1.3 Hz, H-3), 6.05 (d, 1 H, $J_{1,5}$ = 4.4 Hz, H-1), 5.34 (t, 1 H, $J_{4,5}$ = 3 Hz, H-4), 4.60 (pt, 1 H, $J_{5,6}$ = 2.9 Hz, H-6), 4.23 (d, 2 H, CH_2OAc), 3.57 (m, 1 H, H-5), 2.08 (s, 3 H, OAc). Anal. Calcd for $C_8H_{10}O_4$: C, 56.5; H, 5.9. Found: C, 56.5; H, 6.2.

6-(3-Methylbutyl)-2,7-dioxabicyclo[3.2.0]hept-3-ene (4) was prepared in 66.4% yield from 4-methylpentanal and furan according to the method described for oxetane **2**: bp 135 °C (53 Torr); IR 1610 cm^{-1}; ^1H NMR (CCl_4) δ 6.60 (m, 1 H, $J_{3,4}$ = 2.8 Hz, H-3), 6.21 (d, 1 H, $J_{1,5}$ = 4.5 Hz, H-1), 5.27 (t, 1 H, $J_{4,5}$ = 3 Hz, H-4), 4.45 (pt, 1 H, $J_{5,6}$ = 3.2 Hz, H-6), 3.37 (m, 1 H, H-5), signals of the 3-methylbutyl group at 0.9–2.0 (m, 11 H). Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.4; H, 9.6. Found: C, 71.6; H, 9.8.

6,6-Dicarbethoxy-2,7-dioxabicyclo[3.2.0]hept-3-ene (6) was obtained similarly in 30% yield from diethyl ketomalonate and furan. The crude product was purified by column chromatography: IR 1760, 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.56 (m, 1 H, $J_{3,4}$ = 3, $J_{3,5}$ = 1 Hz, H-3), 6.33 (d, 1 H, $J_{1,5}$ = 4.2 Hz, H-1), 5.18 (t, 1 H, $J_{4,5}$ = 2.5 Hz, H-4), 4.26 (m, 5 H, H-5 and two CH_2O), 1.30 (t, 6 H, two CH_3). Anal. Calcd for $C_{11}H_{14}O_6$: C, 54.5; H, 5.8. Found: C, 54.6; H, 6.0.

Oxetanes **1**, **5** and **7** were prepared according to ref 5.

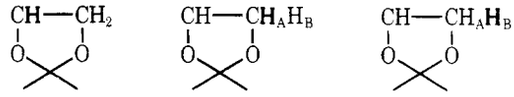
Isomerization of 6-Substituted 2,7-Dioxabicyclo[3.2.0]hept-3-enes. A 1% solution of oxetane **1** (or **2–5**) in diethyl ether or carbon tetrachloride was treated with 0.02–0.04% of *p*-toluenesulfonic acid and left at room temperature for 10–24 h. After neutralization with triethylamine the product was isolated by distillation. Yields, boiling points, and elemental analyses of 3-furylmethanols **8–12** are collected in Table I. All compounds exhibited ^1H NMR low-field signals at δ 7.3–7.4 (2 H) and 6.3–6.4 (1 H) typical for 3-monosubstituted furans. Also their IR spectra displayed bands specific for the furan ring at 1510 and 870–880 cm^{-1}.

Isomerization of 6-substituted 2,7-dioxabicyclo[3.2.0]hept-3-enes with higher concentration of catalyst led to retro cleavage; after addition of 5% *p*-toluenesulfonic acid to compound **5** only benzaldehyde could be detected after 10 h. From oxetane **1** tars were formed under similar conditions. On the other hand, oxetane **6** remained unchanged after standing with 1% hydrogen chloride for 140 h.

3-(1,2-Dihydroxyethyl)furan (13). Butyl 3-furylglycolate (**9**) was reduced with lithium aluminum hydride in ether solution at 0 °C. After typical workup 67% of diol **13** was obtained. The compound solidified after distillation at 110 °C (0.2 Torr): mp 54.5–55 °C; IR 3350, 1510, 875 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.36 (m, 2 H, furan H-2 and H-5), 6.30 (s, 1 H, furan H-4), 4.70 (pd, 1 H, J_{AX} = 4.2, J_{BX} = 6.8 Hz, $CHOHCH_2OH$), 3.65 (m, 2 H, $CHOHCH_2OH$). Anal. Calcd for $C_6H_8O_3$: C, 56.2; H, 6.3. Found: C, 56.3; H, 6.6.

Oxidation of diol **13** with lead tetraacetate in benzene solution gave, after workup, 65% of 3-furylaldehyde, mp of phenylhydrazone 147.5 °C (lit.[7] 149.5°C).

1,2-*O*-Isopropylidene derivative of 3-(1,2-dihydroxyethyl)furan was obtained in 81% yield from **13** and acetone to which a catalytic amount of concentrated sulfuric acid was added: distilled at 45–50 °C (0.2 Torr); IR 1510, 880 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.38 (m, 2 H, furan H-2 and H-4), 6.36 (m, 1 H, furan H-4), 5.00 (pd, 1 H, J_{AX} = 6.0, J_{BX} = 7.8 Hz, fragment a), 4.16 (pd, 1 H, J_{AB} = 7.7 Hz, fragment b),



a b c

3.75 (t, 1 H, fragment c), 1.43 and 1.47 (two s, 6 H, two CH_3). Anal. Calcd for $C_9H_{12}O_3$: C, 64.3; H, 7.1. Found: C, 64.7; H, 7.4.

1-(3-Furyl)-4-methyl-1-pentanone (Perilla Ketone, 15). A solution of 1-(3-furyl)-4-methyl-1-pentanol (**11**, 100 mg) in 3 ml of acetone was treated with Jones reagent[8] until persistent yellow coloration. The excess of the oxidizing reagent was destroyed with a few drops of methanol whereupon the mixture was diluted with 2 ml of water and extracted several times with chloroform. Evaporation of the dried ($MgSO_4$) chloroform solution and distillation of the remaining liquid at 60–70 °C (10 Torr) afforded 61 mg (61.7%) of the perilla ketone: mp of 2,4-dinitrophenylhydrazone 149.5 °C (lit.[9] 149.5 °C); IR 1680, 1570, 1520, 875 cm^{-1}; ^1H NMR (CCl_4) δ 8.67, 7.83, and 6.81 (three m, 3 H, furan H-2, H-4, and H-5), 2.69 (t, 2 H, $J_{2,3}$ = 7.6 Hz, $COCH_2$–), signals of the 2-methylpropyl group at 0.93–1.8 (m, 9 H). Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.3; H, 8.5. Found: C, 72.5; H, 8.7.

Essentially the same result was obtained on oxidation of **11** with Sarett reagent.

Formate of 1-Hydroxy-4-(2-furyl)-1,3-butadiene (16). 6-(2-Furyl)-2,7-dioxabicyclo[3.2.0]hept-3-ene (**7**, 1 g) was chromatographed on a silica gel (Merck) column in a mixture of light petroleum (bp 60–80 °C) and benzene (10:3 v/v). The main fraction (0.63 g) was distilled at 80 °C (0.02 Torr): IR 1730, 1640, 1625, 1555, 1220, 1150, 970, 925, 885, and 738 cm^{-1}; ^1H NMR (CCl_4) δ 8.12 (s, 1 H, HCOO–), 5.43–7.53 (m, 7 H, vinylic and furan H); UV (cyclohexane) λ_{max} 293 nm (ϵ 36 100), 304.5 (45 500), and 317.5 (34 200). Anal. Calcd for $C_9H_8O_3$: C, 65.9; H, 4.9. Found: C, 65.8; H, 4.8.

Registry No.—**1**, 7555-25-1; **2**, 61063-39-6; **3**, 61063-40-9; **4**, 61063-41-0; **5**, 1915-16-8; **6**, 61063-42-1; **7**, 7555-27-3; **8**, 13129-26-5; **9**, 61063-43-2; **10**, 61063-44-3; **11**, 60122-21-6; **12**, 40358-49-4; **13**, 61063-45-4; **13** 1,2-*O*-isopropylidene derivative, 61063-46-5; **14**, 498-60-2; **15**, 553-84-4; **16**, 61063-47-6; *n*-butyl glyoxylate, 6295-06-3; furan, 110-00-9; 4-methylpentanal, 1119-16-0; diethyl ketomalonate, 609-09-6; acetone, 67-64-1.

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Anodic and Chemical Oxidation of 1-Benzyl-3-isochromanone and 1-Benzyl-1,4-dihydro-3(2*H*)-isoquinolone Derivatives

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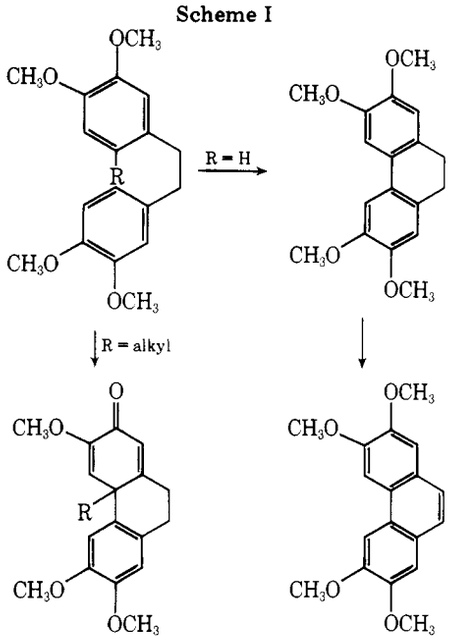
Electrochemical oxidation is a useful method for biaryl coupling of phenols and phenol eithers. These laboratory reactions offer attractive synthetic procedures that parallel a wide range of important biosynthetic processes. Simple me-

thoxy derivatives of bibenzyl undergo intramolecular coupling to afford either dihydrophenanthrenes or the completely aromatic compounds in good yield by electrolysis;[1] but from alkoxybibenzyl compounds with an electron-donating substituent ortho to the ethylene link and para to a methoxy group the principal products have been dienones[2,3] (Scheme I). Several examples are on record in which 1-benzyliso-

Scheme I



quinoline alkaloids have been converted to morphinandienones by anodic oxidation.[4]

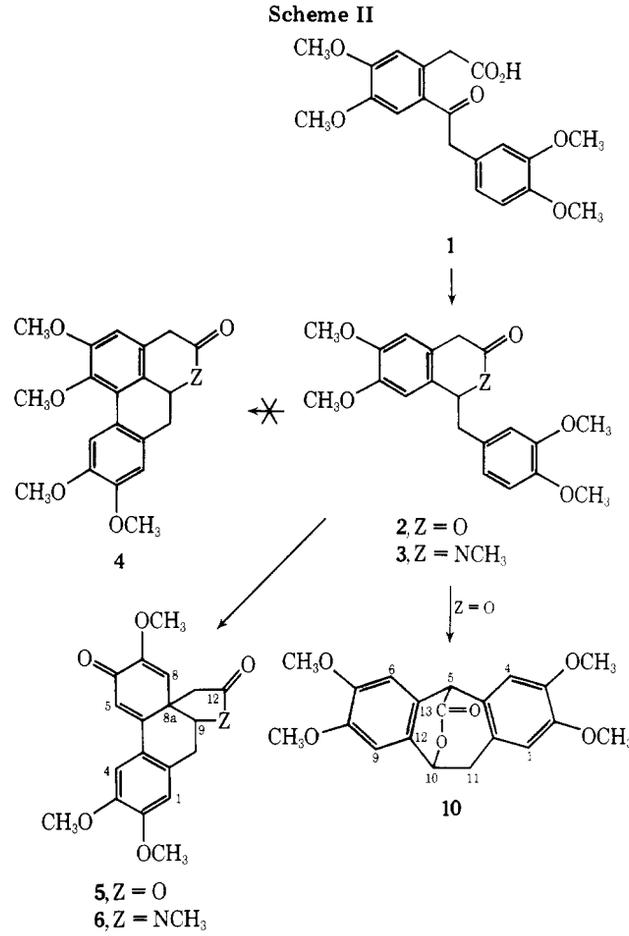
In an earlier communication the keto acid **1** was proposed as a starting compound for a series of isoquinoline alkaloids biogenetically derived from the 1-benzylisoquinolines,[5] and tetrahydropapverine and laudanosine were prepared from **1**. In this study 1-(3,4-dimethoxybenzyl)-6,7-dimethoxy-3-isochromanone (**2**) and 1-(3,4-dimethoxybenzyl)-2-methyl-6,7-dimethoxy-1,4-dihydro-3(2*H*)-isoquinolone (**3**), both prepared from the keto acid **1**, were oxidized electrochemically and also with the chemical oxidant vanadium oxyfluoride. When this work was initiated we supposed that on anodic oxidation of **2** or **3** a simple biaryl coupling would occur with formation of compounds with the aporphine skeleton (**4**).[6] The actual results reported here are more complex than we originally proposed (Scheme II).

The lactone **2** was used as a model compound in these oxidations since the lactone is more easily prepared from the keto acid **1** than the lactam **3**. Anodic oxidation of the lactone **2** has afforded at least two distinct products depending in part on the solvent (and pH) used. Electrolysis of **2** in dichloromethane–trifluoroacetic acid (DCM–TFA)[1] with tetrabutylammonium tetrafluoroborate as supporting electrolyte gave 6,12-dioxo-2,3,7-trimethoxy-6,8a,9,10-tetrahydro-9,8a-epoxyethanophenanthrene (**5**) as the main product in 33% yield. The same spirodienone **5** was isolated in 59% yield from the oxidation of **2** by vanadium oxyfluoride in DCM–TFA solution.

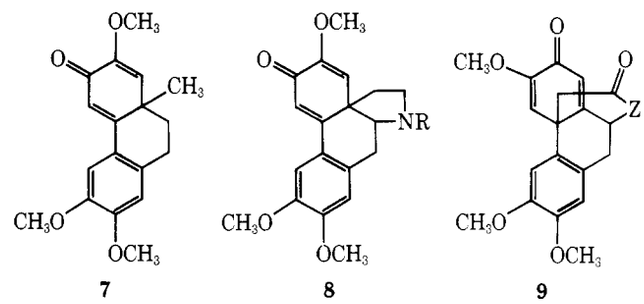
An analogous dienone **6** (6,12-dioxo-2,3,7-trimethoxy-6,8a,9,10-tetrahydro-9,8a-iminoethanophenanthrene) was obtained in approximately 40% yield from the lactam **3**, either by anodic oxidation or vanadium oxyfluoride, when the solvent system DCM–TFA was used.

The constitutions **5** and **6** are supported by elemental composition and spectral data. In both cases the infrared spectra show bands characteristic of the dienone system (1660–1650 and 1630 cm^{-1}); moreover, the positions of the acyl

Scheme II



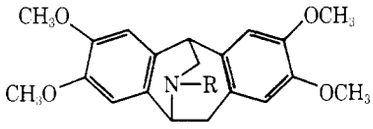
carbonyl bands are shifted to higher wavenumbers in going from **2** to **5** (1740 to 1760 cm^{-1}) or from **3** to **6** (1640 to 1690 cm^{-1}) corresponding to a change from a six- to a five-membered ring in the lactone or lactam, respectively. The NMR spectra are in agreement with the assigned structures, and the UV spectra are helpful in establishing the patterns of conjugation. Compounds **5** and **6** exhibit a similar series of absorption bands in the UV, and the spectra of both compounds correspond closely to those reported for a pair of structurally related conjugated dienones (**7**[3] and **8**[7]). The alternative possibility that **5** or **6** possess a morphinandienone structure (**9**) can be excluded on the basis of the very different UV spectrum described for salutaridine.[8]



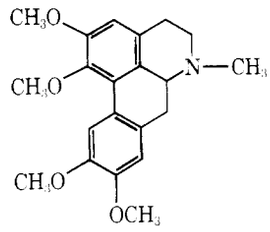
When the isochromanone derivative **2** was oxidized electrolytically in acetonitrile with quaternary ammonium salts, a different product was obtained in 20% yield which is assigned the bridged lactone structure **10**. The formulation of this product as 2,3,7,8-tetramethoxy-13-oxo-10,5-(epoxymethano)dibenzo[*a*,*d*]cycloheptadiene (**10**) rather than a biphenyl derivative (**4**, Z = O) is based on the NMR and UV spectra. In the aromatic region there are three bands at δ 6.77 (1 H), 6.71 (2 H), and 6.48 (1 H) for a total of four hydrogens. In addition to the complex pattern, from interaction of the methylene

hydrogens with the adjacent carbinol hydrogen, that would be present in either **10** or **4** there is a singlet corresponding to one hydrogen at δ 4.41 that can be attributed only to the hydrogen at position 10 in **10.** In the NMR spectrum of the starting lactone **2** there is a singlet for two hydrogens at δ 3.19, and the same spectral feature should persist in the oxidation product if the correct structure were **4** and not **10;** no such band appears in the NMR of the actual product.

When the UV spectrum of the product assigned structure **10** (λ_{max} 289 nm, log ϵ 3.90) is compared with those of *N*-acetylisopavine (**11a,** λ_{max} 287 nm, log ϵ 3.95)[9] and glaucine (**12,** λ_{max} 281 and 302 nm, log ϵ 4.15 and 4.16, respectively)[10]



11a, R = $COCH_3$
b, R = CH_3



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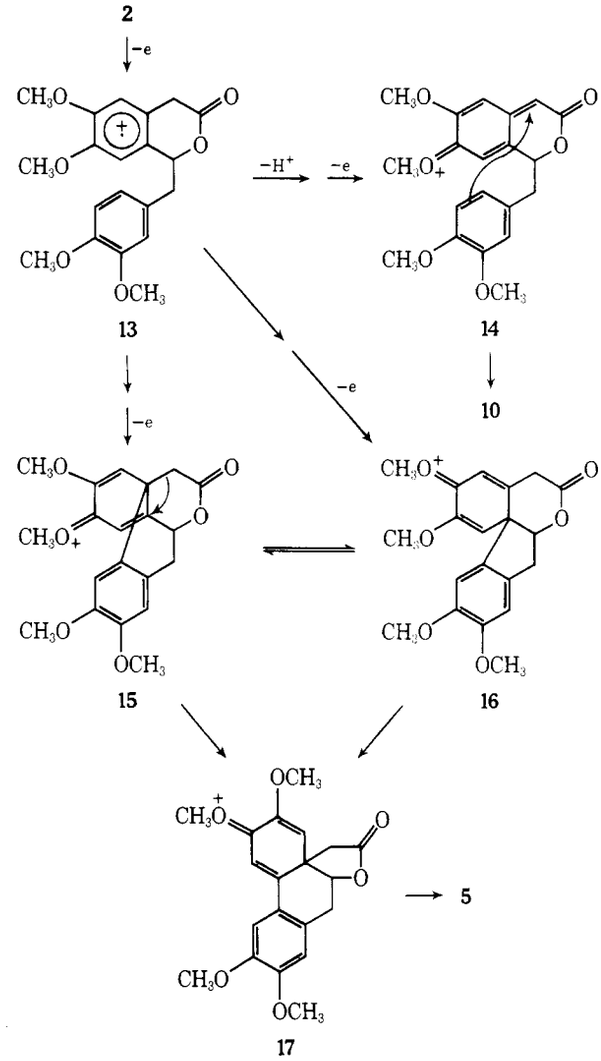
the choice is clearly in favor of the constitution with two isolated dimethoxybenzene rings rather than the tetramethoxybiphenyl system.

The mode of oxidative coupling represented by **10** has not been reported previously from either chemical or electrochemical oxidations of substituted bibenzyls (cf. Scheme I), and this new structural type provides a lactonic analogue of the alkaloid isopavine (**11b**). Although the lactam **3** has also been subjected to anodic oxidation in acetonitrile solution, no nitrogenous product similar to **10** has yet been isolated. We have not established the mechanisms for these reactions, but the formation of **10** from **2** can be rationalized by assuming that a cation radical **13** is generated from **2,** and in neutral or basic solution, and with activation of the adjacent carbonyl group, **13** loses a proton from the 4 position of the isochromanone ring. A second stage of oxidation of the resulting radical would afford the cation **14** which can then serve as an electrophile toward the veratryl ring, leading to **10** (Scheme III). The same intermediate **13** can be invoked to explain the formation of the spirodienone **5.** In acidic solution the loss of a proton would be repressed, and alternatively intramolecular coupling followed by a second oxidation step could occur to give either **15** or **16,** which as a long-lived cation in DCM–TFA[1] could rearrange to the same conjugated dienone **17;** subsequent hydrolysis of **17** would afford **5.**

Scheme III



Experimental Section

General. Melting points were taken on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory. IR and UV spectra were recorded respectively on Perkin-Elmer 337 and Cary 14 spectrophotometers. NMR spectra were obtained on Varian A-60 and HA-100 MHz spectrometers. Electrochemical reactions were carried out in a H-type cell with a sintered glass disk separating the anode and cathode compartments; a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a Model 176 current-to-voltage converter was the power supply. The working and auxillary electrodes were platinum, and silver wire was used as the reference electrode.

1-(3,4-Dimethoxybenzyl)-6,7-dimethoxy-3-isochromanone (2). The keto acid (**1,** 1 g) in ethanol (20 ml) was treated with $NaBH_4$ (0.4 g). After 0.5 h the mixture was heated on a water bath for 10 min, diluted with water (50 ml), and cooled. Addition of 20% HCl to pH 3 and heating quickly gave a colorless solid (0.8 g): mp 174–175 °C (from EtOH); IR 1740 cm^{-1}; *m/e* (M^+) 358; NMR ($CDCl_3$) δ 6775–6.30 (m, 5, ArH), 5.58 (t, 1, J = 5 Hz, ArC**H**RO–), 3.78 (s, 9, OCH_3), 3.62 (s, 3, OCH_3), 3.38–2.48 (m, 4, Ar**C**$\mathbf{H}_2$), 3.19 (s, 2 Ar**C**$\mathbf{H}_2$CO).

Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.03; H, 6.19. Found: C, 67.04; H, 6.28.

6,12-Dioxo-2,3,7-trimethoxy-6,8a,9,10-tetrahydro-9,8a-epoxyethanophenanthrene (5). A. By Anodic Oxidation. The electrolysis vessel was filled with a 4:1 solution of DCM–TFA containing tetrabutylammonium tetrafluoroborate (4.5 g). The lactone (**2,** 0.72 g) was dissolved in the anode compartment, and a potential of 1.3 V was applied for 2.5 h. A deep purple color developed quickly around the anode. The anolyte was stirred for 15 min with Zn dust, but there was no perceptible change in color. The organic solvents were evaporated under reduced pressure, and the residual golden foam was washed with aqueous Na_2CO_3 and then with water. The solid was dissolved in $CHCl_3$–EtOH, and on cooling the spirodienone (**5**) was deposited as a pale yellow solid (0.23 g): mp 286–288 °C; IR 1760 C=O for γ-lactone), 1640, 1630 cm^{-1}; UV max (95% EtOH) 238 nm (log ϵ 4.02), 2.64 (4.12), 290 (3.92), and 357 (3.93); NMR δ 6.96 (s, β H in α, β-unsaturated ketone), 6.76 (s, 1, ArH), 6.49 (s, 1, ArH), 6.03 (s, α H in α,β-unsaturated ketone), 5.05 (t, 1, J = 3.5 Hz, CHO–), 3.95 (s, 6, Ar**OCH**$_3$), 3.78 (s, 3, vinyl OCH_3), 3.08 (d, 2, J = 3.5 Hz, Ar**C**$\mathbf{H}_2$), 2.72 (s, 2, Ar**C**$\mathbf{H}_2CO_2$).

Anal. Calcd for $C_{19}H_{18}O_6$: C, 66.66; H, 5.30. Found: C, 66.69; H, 5.22.

B. By Vanadium Oxyfluoride Oxidation. To a stirred solution of the lactone (**2,** 3.6 g) in DCM (100 ml)–TFA (5 ml) at 0 °C was added a slurry of VOF_3 (5.5 g) in TFA (30 ml). The reaction mixture immediately became dark purple in color. After 5 h the solution was poured into water (400 ml) containing citric acid (12 g). The organic layer was separated, washed with water, and concentrated to afford a red-brown solid. The product **5** was obtained by recrystallization from $CHCl_3$ as ivory crystals, 2.0 g, mp 286–288 °C. This product

proved to be identical with 5 from part A by superimposing the IR spectra.

6,12-Dioxo-2,3,7-trimethoxy-11-methyl-6,8a,9,10-tetrahydro-9,8a-iminoethanophenanthrene (6). A. By Anodic Oxidation. The lactam (**3**, 1.6 g) was electrochemically oxidized in DCM–TFA solution at a constant potential of 1.8 V over a period of 2.5 h. The purple anolyte was treated with Zn dust, filtered, and washed with water (2 × 150 ml), followed by aqueous $NaHCO_3$ (2 × 150 ml). The organic layer was dried (Na_2CO_3), and the solvent was evaporated to leave a brown oil that was redissolved in hot EtOAc–$CHCl_3$. From this solution the lactam spirodienone (**6**) crystallized as a pale yellow solid: 0.6 g; mp 252–254 °C; IR (Nujol) 1690 (C=O for γ-lactam), 1660, 1650 cm^{-1}; UV max (95% EtOH) 239 nm (log ε 4.04), 265 (4.10), 293 (3.92), and 356 (3.89); *m/e* (M^+) 355; NMR δ 6.86 (s, β H in α,β-unsaturated ketone), 6.65 (s, 1, ArH), 6.41 (s, 1, ArH), 5.95 (s, α H in α,β-unsaturated ketone), 3.92 (m, 1, ArC**H**N), 3.84 (s, 6, OCH_3), 3.67 (s, 3, vinyl OCH_3), 2.91 (s, 3, NCH_3), 2.81 (s, 2, ArCH_2CO), 2.78–2.43 (m, 2, ArCH_2).

Anal. Calcd for $C_{20}H_{21}NO_5$: C, 67.59; H, 5.96; N, 3.94. Found: C, 67.72; H, 6.15; N, 4.17.

B. By Vanadium Oxyfluoride Oxidation of 3. A solution of the lactam **3** (3.6 g) in DCM (100 ml) was cooled to 0 °C and treated with a suspension of VOF_3 (5.5 g) in TFA (30 ml). The red-purple solution was stirred for 4 h and then poured into water (400 ml) containing citric acid (12 g). The organic layer was separated and washed with water, dried (Na_2CO_3), and evaporated. The residue (3.6 g was dissolved in MeOH (40 ml)–$CHCl_3$ (15 ml), an the first crop of crystals, 1.4 g, mp 253–255 °C, was identical with the dienone **6** from anodic oxidation of the lactam **3** by infrared spectral comparison.

2,3,7,8-Tetramethoxy-13-oxo-10,5-(epoxymethano)dibenzo[*a,d*]cycloheptadiene (10). A solution of MeCN (230 ml) containing tetrabutylammonium hydrogen sulfate (10 g) was divided between the compartments of the electrolytic cell. The lactone (**2**, 1.79 g) was dissolved in the anolyte. Electrolysis at 1.3 V (vs. Ag reference electrode) for 4 h gave a red-brown solution. The anode solution was evaporated, and the residual brown oil was washed with water to afford an orange solid that was recrystallized from MeOH as colorless crystals: 0.4 g; mp 242–243 °C; IR spectrum (Nujol) 1740 cm^{-1}; UV max (95% EtOH) 285 nm inflection (log ε 3.89), 288 (3.90), 290 (3.89); NMR δ 6.77 (s, 1, ArH), 6.71 (s, 2, ArH), 6.48 (s, 1, ArH), 5.53 (dd, 1, *J* = 7.0, 1.6 Hz, Ar**C**HO–), 4.41 (s, 1, $Ar_2CHC{=}O$), 3.82 and 372 (2 s, 12, OCH_3), 3.62 (dd, 1, *J* = 24, 4.6 Hz), and 3.21 (dd, 1, *J* = 20, 3 Hz); mass spectrum *m/e* (M^+) 356.

Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66; O, 26.94. Found: C, 67.64; H, 5.92; O, 26.99.

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Registry No.—1, 26954-85-8; 2, 61140-40-7; 3, 61140-41-8; 5, 61140-42-9; 6, 61140-43-0; 10, 61140-44-1.

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Baeyer–Villiger-Type Oxidation of an Isoindolo[1,2-*b*][3]benzazepine Derivative

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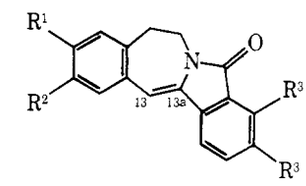
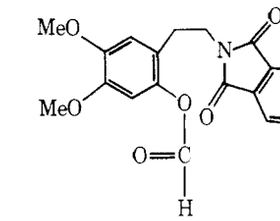
During the course of our work with isoindolo[1,2-*b*][3]-benzazepine derivatives **1a–c**, prepared by a new photo-



1a, $R^1 = R^2 = OMe$; $R^3 = H$
b, $R^1 + R^2 = OCH_2O$; $R^3 = OMe$
c, $R^1 = R^2 = R^3 = OMe$



2

chemical method and correlated with rearrangement products of protoberberine and papaverrubine alkaloids,[3] we investigated routes to C-13–C-13a functionalized derivatives of **1a**. We report on the *m*-chloroperbenzoic acid (MCPBA) oxidation of **1a** to the phthalimide derivative **2**, a reaction which, in sum, is the result of oxidative double bond cleavage and Baeyer–Villiger reaction.

Attempts to prepare the epoxide of **1a** using 1 equiv of MCPBA[4] as well as basic,[5] acidic,[6] and neutral[7] conditions were unsuccessful (see Experimental Section). However, treatment of **1a** with 3 equiv of MCPBA resulted in the formation of **2** in 60% yield. The product showed the molecular formula $C_{19}H_{17}NO_6$ indicating incorporation of three oxygen atoms into compound **1a**. Its IR spectrum showed absorption at 1735 and at 1760 and 1710 cm^{-1} consistent with the presence of formyl ester and phthalimide functionality, respectively. The NMR spectrum exhibited a one-proton singlet at

Scheme I