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Heterocycles. VIII.[1] Syntheses of 12-Acetoxybenzo[*c*]phenanthridines

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The compound obtained from the phenacylimide (**5**) by treatment with *p*-toluenesulfonic acid and ethylene glycol in benzene is the furoisocarbostyril (**7**), in contrast to a previous report. Reduction of **5** with sodium borohydride followed by treatment with hydrochloric acid and then hydrogen chloride affords the styrylisocarbostyril (**10**), photolysis of which provides the benzo[*c*]phenanthridines (**11**) and (**12**), and the amides (**13**) and (**14**). The ethylenedioxyimide (**8**) obtained from **5** affords the styrylisocarbostyrils (**18**) and (**19**) by a similar procedure together with enol acetylation. Photolysis of a mixture of **18** and **19** provides the 12-acetoxybenzo[*c*]phenanthridines (**20**) and (**21**).

Keywords——benzo[*c*]phenanthridines; furo[2,3-*c*]isocarbostyrils; styrylisocarbostyrils; photolysis; NMR (^{1}H and ^{13}C)

We previously reported the syntheses of the 11-acetoxybenzo[*c*]phenanthridines (**2**) and (**3**) from the keto isocarbostyril (**1**) in two steps, as well as the photolysis of **1** to the C-norbenzo[*c*]phenanthridine (**4**).[4] In this connection, we examined synthetic routes to 12-acetoxybenzo[*c*]phenanthridines from the phenacylimide (**5**).

Iida *et al.* recently reported that **5** quantitatively gave the dioxobenzo[*c*]phenanthridine (**6**) on heating with *p*-toluenesulfonic acid (TsOH) and ethylene glycol in benzene.[5] In general, this procedure is used to obtain ethylene ketals, and acidic cyclization of **5** to **6** would not be expected to occur smoothly owing to the presence of a carbonyl group adjacent to the benzene ring. In fact, treatment of **5** with phosphoryl chloride gave no product. We therefore followed the procedure of Iida *et al.*, but obtained results different from theirs, as described below. The phenacylimide (**5**) afforded the furoisocarbostyril (**7**) (84%) under their conditions, whereas the ethylenedioxyimide (**8**) was obtained in 68% yield under similar conditions when the water formed was removed by azeotropic distillation. The infrared (IR) spectrum of **7** shows the carbonyl band of a lactam group at 1649 cm^{-1}, and the proton magnetic resonance (^{1}H NMR) spectrum exhibits a one-proton singlet (δ 6.93) due to the proton of the furan ring, in addition to signals for seven aromatic protoons. Eight singlet carbons and eight doublet carbons including one carbon (δ 99.6) of the furan ring are observed in the aromatic region in the ^{13}C NMR spectrum of **7**. These spectral properties are in accord with those of the structure shown for **7**, rather than **6**. Acidic hydrolysis of **7** afforded **5** in 64% yield, supporting the above conclusion. Enolization of the carbonyl group at the 3- or 2″-position, addition of the hydroxyl group to the remaining carbonyl group and dehydration probably lead to the formation of **7** from **5**. The structure of **8** is also established on the basis of its spectral data (see "Experimental"). Treatment of **8** with TsOH and ethylene glycol in benzene provided **7**. The presence of water in the ethylene glycol used would result in the conversion of **8** into **5** which affords **7** *via* the above pathway. The Bischler-Napieralski reaction of **8** gave **5** (58%) under

1) Part VII: Y. Harigaya, T. Suzuki, and M. Onda, *Chem. Pharm. Bull.*, **27**, 2636 (1979).
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4) M. Onda, Y. Harigaya, and T. Suzuki, *Chem. Pharm. Bull.*, **25**, 2935 (1977).
5) H. Iida, H. Ina, and T. Kikuchi, Abstracts of the 10th Congress of Heterocyclic Chemistry, University of Tsukuba, Japan, October, 1977, p. 191.

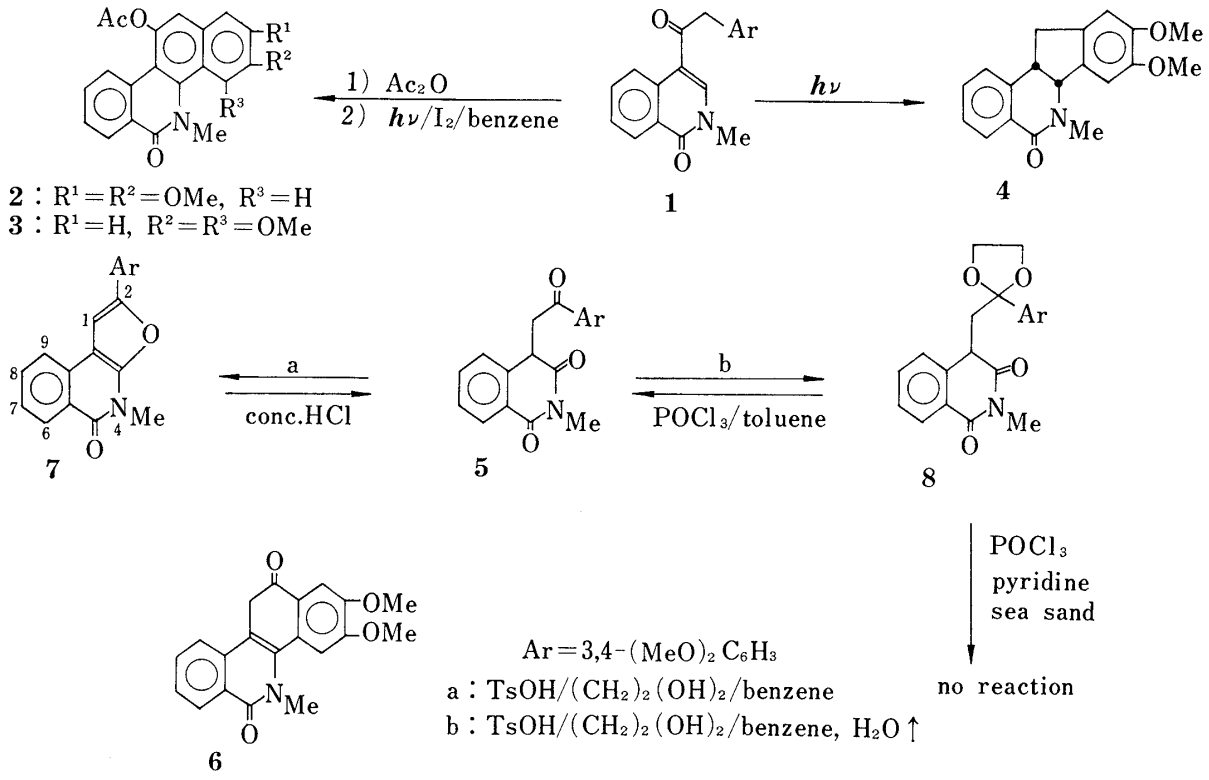


Chart 1

the usual conditions (phosphoryl chloride/toluene) and no compound under modified conditions (phosphoryl chloride/pyridine/sea sand).[6]

We next investigated the photolyses of styrenes derived from **5** and **8** to obtain benzo[*c*]-phenanthridines. On reduction with sodium borohydride in chloroform/methanol followed by treatment with 10% hydrochloric acid, **5** gave the methoxyisocarbostyril (**9**) (95%) which showed the methyl signal of a newly introduced methoxyl group at δ 3.17 in the ^{1}H NMR spectrum. Further, treatment of **9** with hydrogen chloride afforded the styrylisocarbostyril (**10**) (70%), the structure of which was confirmed to have the *E* configuration by the coupling constant (16 Hz) between two vinylic protons in the ^{1}H NMR spectrum.

Photolysis of **10** in the presence of iodine afforded the benzo[*c*]phenanthridines (**11**) (16%) and (**12**) (19%), and the amides (**13**) (20%) and (**14**) (21%). The structures of **11** and **12** are assigned on the basis of the characteristic methyl signals of methoxyl and N-methyl groups in their ^{1}H NMR spectra (see "Experimental").[4] The ^{1}H NMR spectra show a two-proton singlet for the 1- and 4-H's at δ 7.14 in **13**, and a one-proton doublet for the 8-H at δ 8.16 (J 2 Hz) in **14**, establishing the structures shown. Since **11** and **12** were not photochemically converted into **13** and **14** under the above conditions, it is thought that the intermediate (**15**) obtained from **10** may give **13** and **14** *via* C–N bond fission (→**16**) followed by a hydrogen shift.

The ethylenedioxyimide (**8**) was converted into the phenacylisocarbostyril (**17**) (79%) on reduction with sodium borohydride followed by treatment with conc. hydrochloric acid. Photolysis of **17** provided no product, in contrast to that of **1**. Treatment of **17** with isopropenyl acetate and TsOH in refluxing benzene gave a mixture of the *Z*-styrylisocarbostyril (**18**) and *E*-isomer (**19**) (73%) in a ratio of 3: 1 on the basis of the methyl signal intensities of acetoxy groups in the ^{1}H NMR spectrum. Assignment of each methyl group in the ^{1}H NMR spectra of **18** and **19**, which were separated by preparative thin-layer chromatography (prep.

6) N. Itoh and S. Sugasawa, *Tetrahedron*, **6**, 16 (1959).

TLC), is performed. The styrylisocarbostyrils (**18**) and (**19**) have a double bond with three bulky substituents, resulting in loss of their coplanarity owing to steric interaction. Judging from their stereostructures, it is thought that only one ring (isocarbostyril) in **18** is forced out of coplanarity with respect to the double bond, whereas two rings in **19** are not coplanar. Thus, the protons of **19**, which resonate at higher fields than do the corresponding ones in **18**,

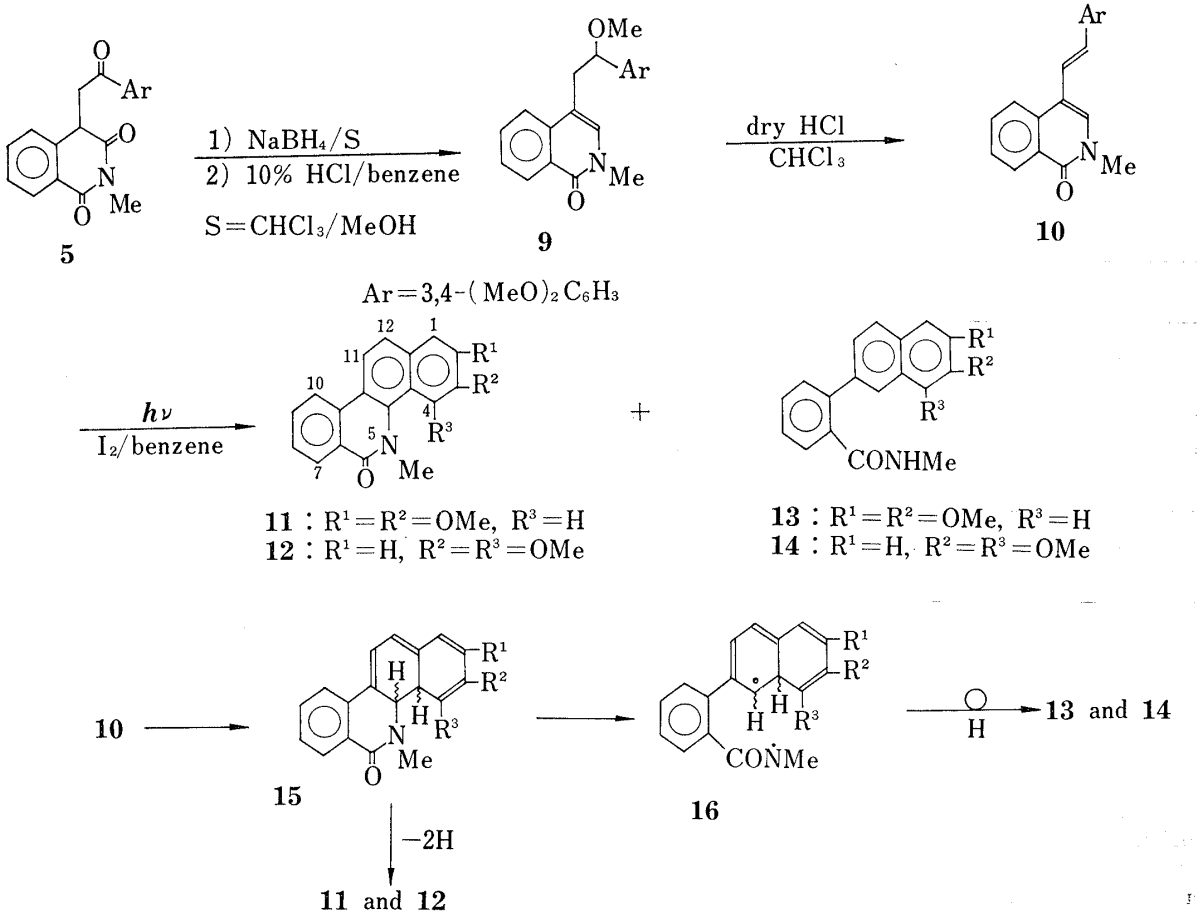
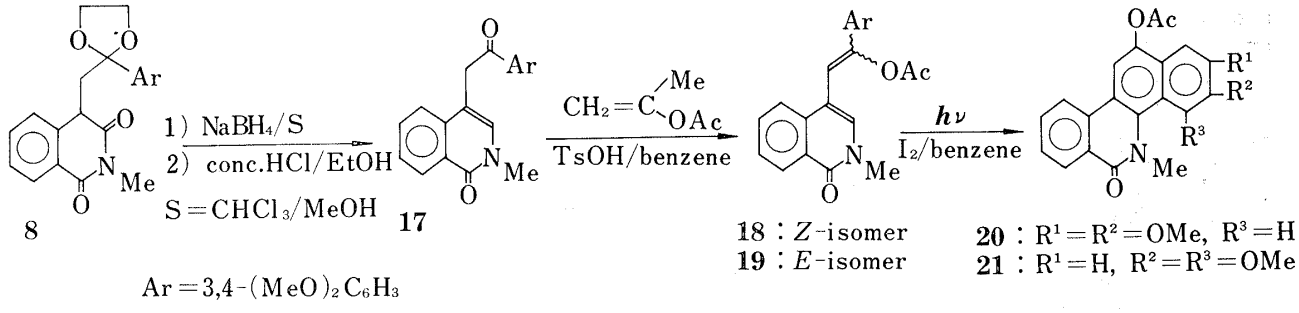


Chart 2



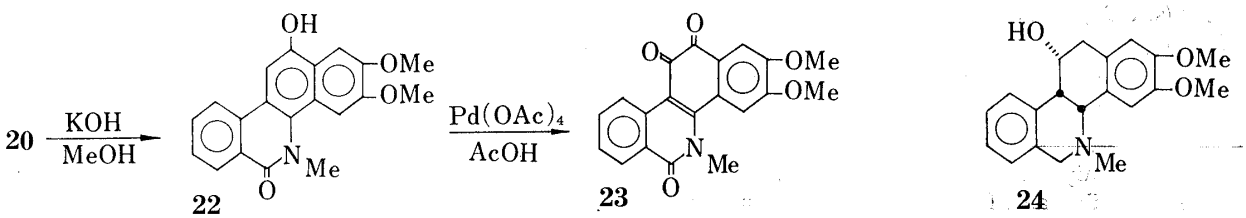


Chart 3

are influenced by the mutually anisotropic effects of both rings, while an up-field shift of the methyl resonance of the 2″-OAc group in **18** is caused by the effect of the isocarbostyril moiety (Table I).

Photolysis of a mixture of **18** and **19** in the presence of iodine gave the 12-acetoxybenzo[*c*]phenanthridines (**20**) (37%)[7] and (**21**) (30%). Their ^{1}H NMR spectra show the characteristic methyl signals of methoxyl and N-methyl groups, and structures are assigned by comparison of the spectra with those of related compounds.[4]

Hydrolysis of **20** with methanolic potassium hydroxide quantitatively gave the 12-hydroxybenzo[*c*]phenanthridine (**22**), which was converted into the trioxobenzo[*c*]phenanthridine (**23**) (82%)[4,7] on oxidation with lead tetraacetate. The synthesis of an analog (**24**) of chelidonine from **23** *via* several steps has been reported.[7]

Table I. ^{1}H NMR Data for **18** and **19**

	2-Me	3-H	5-H	6-H	7-H	8-H
18	3.60	7.08		7.73—7.40		8.47, dd
19	3.43	6.85, d	7.74, dt	7.66, dt[a]	7.49, dt[a]	8.45, dd

	2′-H	3′-OMe	4′-OMe	5′-H	6′-H	1″-H	2″-OCOMe
18	7.26, d	3.93,	3.90	6.90, d	7.13, dd	6.65	2.14
19	6.73, d	3.80	3.47	6.67, d	6.84, dd	6.32, d	2.27

J_{ortho} 8 Hz, J_{meta} 2 Hz (**18** and **19**) $J_{3,1''}$ 2 Hz (**19**).
a) These assignments may be reversed.

Experimental

Melting points were determined on a micro hot-stage apparatus and are uncorrected. IR spectra were recorded on a JASCO IR-G spectrometer in chloroform unless otherwise mentioned. ^{1}H and ^{13}C NMR spectra were taken on a JEOL JNM PS-100 spectrometer at 100 and 25.1 MHz, respectively, in deuteriochloroform. Mass spectra (MS) were measured with a JEOL JMS-OIS spectrometer. Photolyses were performed with a 100 W medium pressure mercury lamp under nitrogen at room temperature.

4-(3,4-Dimethoxyphenacyl)-2-methylhomophthalimide (**5**)——The phenacylimide (**5**) was prepared by the procedure described in the literature,[8] modified by hydrogenation over 10% Pd-C in ethyl acetate at the final stage. Colorless prisms of mp 159.5—160° (from methanol). IR ν_{max} cm^{-1}: 1713, 1663 (O=CNC=O and C=O). ^{1}H NMR δ: 8.26 (1H, dd, *J* 8 and 2 Hz, 8-H), 7.56 (1H, dd, *J* 8 and 2 Hz, 5-H), 7.50 (1H, dt, *J* 8 and 2 Hz, 6-H),[9] 7.43 (1H, dt, *J* 8 and 2 Hz, 7-H),[9] 7.39 (1H, d, *J* 2 Hz, 2′-H), 7.24 (1H, dd, *J* 8 and 2 Hz, 6′-H), 6.85 (1H, d, *J* 8 Hz, 5′-H), 4.28 (1H, t, *J* 4.5 Hz, 4-H), 3.96 (2H, d, *J* 4.5 Hz, 1″-H$_2$), 3.90, 3.83 (3H each, s, 3′- and 4′-OMe's), 3.39 (3H, s, 2-Me). *Anal.* Calcd for $C_{20}H_{19}NO_5$: C, 68.05; H, 5.43; N, 3.96. Found: C, 68.29; H, 5.41; N, 3.82.

2-(3,4-Dimethoxyphenyl)-4-methylfuro[2,3-*c*]isocarbostyril (**7**)——A solution of **5** (3.4 g), ethylene glycol (30 ml) and TsOH (1.9 g) in anhyd. benzene (250 ml) was refluxed for 15 hr. The reaction mixture was washed with water, 10% aq. $NaHCO_3$ and saturated aq. NaCl, and then dried over Na_2SO_4. Work-up gave **7** (2.7 g, 84%) as colorless needles of mp 179—180° (from methanol). IR ν_{max} cm^{-1}: 1649 (NC=O). ^{1}H NMR δ: 8.41 (1H, dd, *J* 8 and 2 Hz, 6-H), 7.69—7.34 (3H, m, 7-, 8- and 9-H's), 7.20 (1H, dd, *J* 8 and 2 Hz, 6′-H), 7.11 (1H, d, *J* 2 Hz, 2′-H), 6.93 (1H, s, 1-H), 6.87 (1H, d, *J* 8 Hz, 5′-H), 3.93, 3.88 (3H each, s, 3′- and 4′-OMe's), 3.72 (3H, s, 4-Me). ^{13}C NMR δ: 160.9 (s, C-5), 149.4 (s, C-3′), 149.3 (s, C-4′), 148.8 (s, C-3a), 147.9 (s, C-2), 132.4 (d, C-8), 131.5 (s, C-9a), 129.2 (d, C-6), 124.9 (d, C-7), 123.0, 122.9 (s each, C-5a and -1′), 116.1 (d, C-6′), 111.5 (d, C-5′), 106.7 (d, C-2′), 101.6 (s, C-9b), 99.6 (d, C-1), 56.0 (q, 3′- and 4′-OMe's), 28.6 (q, 4-Me). *Anal.* Calcd for $C_{20}H_{17}NO_4$: C, 71.62; H, 5.12; N, 4.18. Found: C, 71.86; H, 5.12; N, 4.19. MS *m/e*: M$^+$, 335.115 (M, 335.116).

7) I. Ninomiya, O. Yamamoto, and T. Naito, *Heterocycles*, **7**, 131 (1977).
8) A.S. Bailey and D.L. Swallow, *J. Chem. Soc.*, **1956**, 2477.
9) These assignments may be reversed.

Hydrolysis of 7——A solution of **7** (20 mg) in conc. HCl (1 ml) was heated at 90—100° for 3.5 hr. After dilution with water, the precipitate was collected and recrystallized from methanol to yield **5** (13.5 mg, 64%) as colorless prisms of mp 158—159°.

4-[2-(3,4-Dimethoxyphenyl)-2-ethylenedioxyethyl]-2-methylhomophthalimide (8)——A solution of **5** (1.0 g), ethylene glycol (8 ml) and TsOH (134 mg) in anhyd. benzene (100 ml) was refluxed with removal of water by slow azeotropic distillation for 18 hr. Work-up afforded **8** (768 mg, 68%) as colorless prisms of mp 150—151° (from methanol). IR ν_{max} cm^{-1}: 1713, 1663 (O=CNC=O). ^{1}H NMR δ: 8.13 (1H, dd, J 8 and 2 Hz, 8-H), 7.59—7.25 (3H, m, 5-, 6- and 7-H's), 6.84 (1H, dd, J 8 and 2 Hz, 6′-H), 6.79 (1H, d, J 2 Hz, 2′-H), 6.71 (1H, d, J 8 Hz, 5′-H), 4.02 (1H, dd, J 5 and 4 Hz, 4-H), 3.93—3.19 (4H, m, 2″-OCH_2CH_2O), 3.80 (6H, s, 3′- and 4′-OMe's), 3.35 (3H, s, 2-Me), 2.97 (1H, dd, J 15 and 4 Hz, 1″-H), 2.77 (1H, dd, J 15 and 5 Hz, 1″-H). *Anal.* Calcd for $C_{22}H_{23}NO_6$: C, 66.48; H, 5.85; N, 3.53. Found: C, 66.30; H, 5.92; N, 3.45.

Reaction of 8 with Phosphoryl Chloride——A solution of **8** (100 mg) and $POCl_3$ (0.2 ml) in anhyd. toluene (5 ml) was heated at 80° for 7 hr. Work-up gave **5** (52 mg, 58%) as colorless prisms of mp 153—154.5° (from methanol).

4-[2-(3,4-Dimethoxyphenyl)-2-methoxyethyl]-2-methylisocarbostyril (9)——$NaBH_4$ (100 mg) was added to a solution of **5** (101 mg) in chloroform/methanol (1/1, v/v) (4 ml). The mixture was stirred at room temperature for 30 min and then evaporated down *in vacuo*. The residue was dissolved in benzene (3 ml). After addition of 10% HCl (1.5 ml), the mixture was stirred at room temperature for 3.5 hr. Work-up gave an oil, and prep. TLC (silica gel plates; ethyl acetate) provided **9** (96 mg, 95%), *Rf* 0.35, as a colorless oil. IR ν_{max} cm^{-1}: 1647 (NC=O). ^{1}H NMR δ: 8.45 (1H, dd, J 8 and 2 Hz, 8-H), 7.73—7.35 (3H, m, 5-, 6- and 7-H's), 6.76 (1H, d, J 2 Hz, 2′-H), 6.75 (1H, d, J 8 Hz, 5′-H), 6.68 (1H, dd, J 8 and 2 Hz, 6′-H), 6.67 (1H, s, 3-H), 4.28 (1H, dd, J 7 and 6 Hz, 2″-H), 3.85, 3.82 (3H each, s, 3′- and 4′-OMe's), 3.47 (3H, s, 2-Me), 3.17 (3H, s, 2″-OMe), 3.13 (1H, dd, J 14 and 7 Hz, 1″-H), 2.88 (1H, dd, J 14 and 6 Hz, 1″-H). MS m/e: M$^+$, 353.163. Calcd for $C_{21}H_{23}NO_4$: M, 353.163.

(*E*)-4-(3,4-Dimethoxystyryl)-2-methylisocarbostyril (10)——Dry HCl was passed through a solution of **9** (76 mg) in anhyd. chloroform (10 ml) with cooling for 20 min until the solution was saturated. After standing at room temperature for 24 hr, the reaction mixture was washed with 10% aq. Na_2CO_3 and water, and then dried over Na_2SO_4. Work-up gave an oil, and prep. TLC (silica gel plates; benzene/ethyl acetate=1/1, v/v) afforded **10** (48 mg, 70%), *Rf* 0.50, as colorless granules of mp 132—133° (from ethanol). IR ν_{max} cm^{-1}: 1644 (NC=O). ^{1}H NMR δ: 8.49 (1H, dd, J 8 and 2 Hz, 8-H), 7.80 (1H, dd, J 8 and 2 Hz, 5-H), 7.66 (1H, dt, J 8 and 2 Hz, 6-H),[9] 7.49 (1H, dt, J 8 and 2 Hz, 7-H),[9] 7.27 (1H, s, 3-H), 7.16, 6.81 (1H each, d, J 16 Hz, 1″- and 2″-H's), 7.06 (1H, d, J 2 Hz, 2′-H), 7.04 (1H, dd, J 8 and 2 Hz, 6′-H), 6.85 (1H, d, J 8 Hz, 5′-H), 3.92, 3.88 (3H, each, s, 3′- and 4′-OMe's), 3.62 (3H, s, 2-Me). *Anal.* Calcd for $C_{20}H_{19}NO_3$: C, 74.75; H, 5.96; N, 4.36. Found: C, 74.54; H, 5.95; N, 4.37. MS m/e: M$^+$, 321.138 (M, 321. 137).

5,6-Dihydro-2,3-dimethoxy-5-methyl-6-oxobenzo[*c*]phenanthridine (11), 5,6-Dihydro-3,4-dimethoxy-5-methyl-6-oxobenzo[*c*]phenanthridine (12), 2,3-Dimethoxy-6-[*o*-(N-methylcarbamoyl)phenyl]naphthalene (13) and 1,2-Dimethoxy-7-[*o*-(N-methylcarbamoyl)phenyl]naphthalene (14)——A solution of **10** (50.5 mg) and I_2 (5 mg) in anhyd. benzene (140 ml) was irradiated for 15 min. Work-up gave an oil, which was purified by prep. TLC (silica gel plates; benzene/ethyl acetate=4/1, v/v) to afford **11** (8 mg, 16%), **12** (9.6 mg, 19%), **13** (10.1 mg, 20%) and **14** (10.5 mg, 21%).

The Benzo[*c*]phenanthridine (**11**): Colorless prisms of mp 199—200° (from ethanol), *Rf* 0.55. IR ν_{max} cm^{-1}: 1638 (NC=O). ^{1}H NMR δ: 8.53 (1H, dd, J 8 and 2 Hz, 7-H), 8.25 (1H, br d, J 8 Hz, 10-H), 8.10 (1H, d, J 9 Hz, 11-H), 7.76 (1H, dt, J 8 and 2 Hz, 9-H), 7.60 (1H, s, 4-H), 7.59 (1H, d, J 9 Hz, 12-H), 7.56 (1H, dt, J 8 and 2 Hz, 8-H), 7.18 (1H, s, 1-H), 4.06 (9H, s, 2-, 3-OMe's and 5-Me). *Anal.* Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.38. Found: C, 74.96; H, 5.33; N, 4.47. MS m/e: M$^+$, 319.121 (M, 319.121).

The Benzo[*c*]phenanthridine (**12**): Colorless prisms of mp 188—189° (from ethanol), *Rf* 0.60. IR ν_{max} cm^{-1}: 1634 (NC=O). ^{1}H NMR δ: 8.60 (1H, dd, J 8 and 2 Hz, 7-H), 8.27 (1H, br d, J 8 Hz, 10-H), 8.06 (1H, d, J 9 Hz, 11-H), 7.80 (1H, dt, J 8 and 2 Hz, 9-H), 7.63 (1H, dt, J 8 and 2 Hz, 8-H), 7.63 (1H, d, J 9 Hz, 12-H), 7.55 (1H, d, J 9 Hz, 1-H), 7.37 (1H, d, J 9 Hz, 2-H), 4.02 (3H, s, 3-OMe), 3.75 (3H, s, 4-OMe), 3.52 (3H, s, 5-Me). *Anal.* Calcd for $C_{20}H_{17}NO_3$: C, 75.22; H, 5.37; N, 4.38. Found: C, 74.97; H, 5.36; N, 4.22. MS m/e: M$^+$, 319.123 (M, 319.121).

The Amide (**13**): A colorless oil, *Rf* 0.32. IR ν_{max} cm^{-1}: 3480 (NH), 1645 (NC=O). ^{1}H NMR δ: 7.73—7.66 (3H, m, aromatic H's), 7.45—7.31 (4H, m, aromatic H's), 7.14 (2H, s, 1- and 4-H's), 5.20 (1H, br s, NH),[10] 4.01, 3.99 (3H each, s, 2- and 3-OMe's), 2.61 (3H, d, J 5 Hz, NHMe).[11] MS m/e: M$^+$, 321.136. Calcd for $C_{20}N_{19}NO_3$: M, 321.136.

The Amide (**14**): A colorless oil, *Rf* 0.36. IR ν_{max} cm^{-1}: 3470 (NH), 1651 (NC=O). ^{1}H NMR δ: 8.16 (1H, d, J 2 Hz, 8-H), 7.83—7.33 (8H, m, aromatic H's), 5.28 (1H, br s, NH),[10] 4.01, 3.99 (3H each, s, 1- and 2-OMe's), 2.65 (1H, d, J 5 Hz, NHMe).[11] MS m/e: M$^+$, 321.136. Calcd for $C_{20}H_{19}NO_3$: M, 321.136.

4-(3,4-Dimethoxyphenacyl)-2-methylisocarbostyril (17)——A solution of **8** (890 mg) and $NaBH_4$ (1.1 g) in chloroform/methanol (1/1, v/v) (25 ml) was stirred at room temperature for 1 hr. After concentration

10) On addition of D_2O this signal disappeared.
11) On addition of D_2O this signal coalesced into a singlet.

in vacuo, the residue was dissolved in chloroform, washed with water and then dried over Na_2SO_4. The residue obtained from the chloroform solution was dissolved in conc. HCl/ethanol (1/10, v/v) (10 ml) and heated at 60° for 10 min. Work-up gave **17** (599 mg, 79%) as light yellow needles of mp 198—200° (from ethanol). IR ν_{max} cm^{-1}: 1654 (NC=O and C=O). ^{1}H NMR δ: 8.49 (1H, dd, *J* 8 and 2 Hz, 8-H), 7.73 (1H, dd, *J* 8 and 2 Hz, 5-H), 7.57 (1H, d, *J* 2 Hz, 2′-H), 7.54 (2H, dt, *J* 8 and 2 Hz, 6- and 7-H's), 7.39 (1H, dd, *J* 8 and 2 Hz, 6′-H), 6.96 (1H, s, 3-H), 6.93 (1H, d, *J* 8 Hz, 5′-H), 4.27 (2H, s, 1″-H_2), 3.95, 3.89 (3H each, s, 3′- and 4′-OMe's), 3.56 (3H, s, 2-Me). *Anal.* Calcd for $C_{20}H_{19}NO_4$: C, 71.19; H, 5.69; N, 4.15. Found: C, 70.95; H, 5.58; N, 4.41. MS *m/e*: M$^+$, 337.131 (M, 337.128).

(*Z*)-4-(*β*-Acetoxy-3,4-dimethoxystyryl)-2-methylisocarbostyril (18) and the *E*-Isomer (19)——A solution of **17** (244 mg), isopropenyl acetate (3 ml) and TsOH (30 mg) in anhyd. benzene (10 ml) was refluxed for 3 hr, and then concentrated *in vacuo*. The residue was dissolved in a solution of isopropenyl acetate (1 ml) and TsOH (20 mg) in anhyd. benzene (8 ml). The mixture was refluxed for 3 hr and then concentrated *in vacuo* as before. This procedure was repeated three times. Work-up gave an oil, and prep. TLC (silica gel plates; benzene/ethyl acetate=1/1, v/v) yielded a mixture of **18** and **19** (200 mg, 73%) in a ratio of 3:1 from the zone with *Rf ca.* 0.40. Further, prep. TLC of the above mixture (80 mg) afforded **18** (43 mg) and **19** (17 mg) from the zones with *Rf* 0.39 and 0.43, respectively.

The *Z*-Isomer (**18**): Colorless prisms of mp 155—157° (from ethanol). IR ν_{max} cm^{-1}: 1759 (OC=O), 1647 (NC=O). ^{1}H NMR (Table I). *Anal.* Calcd for $C_{22}H_{21}NO_5$: C, 69.65; H, 5.58; N, 3.69. Found: C, 69.41; H, 5.53; N, 3.59. MS *m/e*: M$^+$, 379.144 (M, 379.142).

The *E*-Isomer (**19**): Colorless prisms of mp 147—149° (from ethanol). IR ν_{max} cm^{-1}: 1760 (OC=O), 1642 (NC=O). ^{1}H NMR (Table I). *Anal.* Calcd for $C_{22}H_{21}NO_5 \cdot 1/3H_2O$: C, 68.56; H, 5.67; N, 3.63. Found: C, 68.68; H, 5.67; N, 3.56. MS *m/e*: M$^+$, 379.139 (M, 379.142).

12-Acetoxy-5,6-dihydro-2,3-dimethoxy-5-methyl-6-oxobenzo[*c*]phenanthridine (20) and 12-Acetoxy-5,6-dihydro-3,4-dimethoxy-5-methyl-6-oxobenzo[*c*]phenanthridine (21)——A solution of a mixture of **18** and **19** (110 mg) and I_2 (23 mg) in anhyd. benzene (170 ml) was irradiated for 16 min. Work-up gave an oil, and prep. TLC (silica gel plates; benzene/ethyl acetate=2/1, v/v) afforded **20** (40.4 mg, 37%) and **21** (32.7 mg, 30%).

The 12-Acetoxybenzo[*c*]phenanthridine (**20**): Colorless needles of mp 203—204° (from ethanol), *Rf* 0.22. IR ν_{max} cm^{-1}: 1766 (OC=O), 1640 (NC=O). ^{1}H NMR δ: 8.51 (1H, dd, *J* 8 and 2 Hz, 7-H), 8.11 (1H, dd, *J* 8 and 2 Hz, 10-H), 7.88 (1H, s, 11-H), 7.72 (1H, dt, *J* 8 and 2 Hz, 9-H), 7.57 (1H, s, 4-H), 7.55 (1H, dt, *J* 8 and 2 Hz, 8-H), 7.13 (1H, s, 1-H), 4.01 (9H, s, 2-, 3-OMe's and 5-Me), 2.50 (3H, s, 12-OCOMe). *Anal.* Calcd for $C_{22}H_{19}NO_5 \cdot 1/5H_2O$: C, 69.36; H, 5.13; N, 3.68. Found: C, 69.32; H, 5.04; N, 3.50. MS *m/e*: M$^+$, 377.127 (M, 377.126).

The 12-Acetoxybenzo[*c*]phenanthridine (**21**): Colorless prisms of mp 158—160° (from ether/hexane), *Rf* 0.42. IR ν_{max} cm^{-1}: 1760 (OC=O), 1637 (NC=O). ^{1}H NMR δ: 8.58 (1H, dd, *J* 8 and 2 Hz, 7-H), 8.13 (1H, dd, *J* 8 and 2 Hz, 10-H), 7.83 (1H, s, 11-H), 7.76 (1H, dt, *J* 8 and 2 Hz, 9-H), 7.64 (1H, d, *J* 9 Hz, 1-H), 7.60 (1H, dt, *J* 8 and 2 Hz, 8-H), 7.37 (1H, d, *J* 9 Hz, 2-H), 4.02 (3H, s, 3-OMe), 3.74 (3H, s, 4-OMe), 3.54 (3H, s, 5-Me), 2.50 (3H, s, 12-OCOMe). *Anal.* Calcd for $C_{22}H_{19}NO_5$: C, 70.01; H, 5.07; N, 3.71. Found: C, 69.81; H, 5.08; N, 3.57. MS *m/e*: M$^+$, 377.129 (M, 377.126).

5,6-Dihydro-2,3-dimethoxy-12-hydroxy-5-methyl-6-oxobenzo[*c*]phenanthridine (22)——A solution of **20** (54 mg) in 1% KOH/methanol (12 ml) was stirred at room temperature for 5 min. After concentration *in vacuo*, the residue was acidified with 10% HCl and extracted with chloroform. Work-up gave **22** (48 mg) quantitatively as light yellow prisms of mp 274—275°, *Rf* 0.52 (silica gel plates; benzene/ethyl acetate=1/2, v/v). IR ν_{max}^{KBr} cm^{-1}: 3425, 3230 (OH), 1612 (NC=O). MS *m/e*: M$^+$, 335.119. Calcd for $C_{20}H_{17}NO_4$: M, 335.116. Because of its insolubility in common solvents, **22** was used for the next reaction without recrystallization.

2,3-Dimethoxy-5-methyl-5,6,11,12-tetrahydro-6,11,12-trioxobenzo[*c*]phenanthridine (23)——A solution of **22** (20 mg) and $Pb(OAc)_4$ (117 mg) in acetic acid (3 ml) was stirred at room temperature for 20 min. Water was then added for extraction with chloroform. The chloroform solution was washed with 10% aq. Na_2CO_3 and water, and then dried over Na_2SO_4. Work-up afforded **23** (17 mg, 82%) as violet prisms of mp>300° (from benzene). IR ν_{max} cm^{-1}: 1698 (O=CC=O), 1648 (NC=O). MS *m/e*: M$^+$, 349.095. Calcd for $C_{20}H_{15}NO_5$: M, 349.095. The trioxobenzo[*c*]phenanthridine (**23**) was identical with an authentic sample[4] as determined by comparison of the IR spectra.