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Heterocycles. IV.[1] Photolyses of the 4-Arylacetylated 1,2-Dihydroisoquinoline, Isocarbostyril and Its Enol Acetates

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In order to obtain the 11-oxygenated benzo[*c*]phenanthridines photolyses of the 1,2-dihydroisoquinoline (1), the isocarbostyril (3) and its enol acetates (7) and (8) are examined. The 1,2-dihydroisoquinoline (1) and the isocarbostyril (3) do not give the expected compounds. The enol acetates (7) and (8) afford the 11-acetoxybenzo[*c*]phenanthridines (10) and (11). On hydrolysis and successive oxidation, 10 affords the quinone (13) which is thought to be an intermediate for synthesis of the chelidonine-like compound.

Keywords——4-styrylisocarbostyril; benzo[*c*]phenanthridine; photochemistry; NMR; NOE

The syntheses of the 11-hydroxybenzo[*c*]phenanthridines possessing the saturated C ring have been carried out by two groups.[3] These synthetic routes consist of constitution of the framework, introduction of the Δ^{11}-bond and its epoxidation. A straight synthesis may be achieved from the 4-arylacetylisoquinolines. It was found, however, that the attempted cyclization of the 1,2-dihydroisoquinoline (**1**) was unsuccessful.[4] We have examined photocyclizations of **1**, the isocarbostyril (3) and its isomeric enol acetates (7) and (**8**). We herein wish to report, in full, the results, which have been described in our preliminary communication,[5] together with the others obtained.

It has been known that benzyl 1-cyclohexeny ketone was smoothly photocyclized to give 1,2,3,4,4a,10a-hexahydro-10-phenanthrone.[6] Although **1** is similar to the above ketone, quite different results were obtained. Photolysis of **1** in methanol in the presence of boron trifluoride etherate afforded the *pri*-carbinol (2) in 48% yield. Its proton magnetic resonance (PMR) shows the signal for the 1-H at δ 4.44 as sextet (J 5 and 1.5 Hz[7]) and the ones for the CH_2 of the CH_2OH group at δ 3.69 and 3.58 as AB quartet (J 11 and 5 Hz). Photolysis of **1** in acetone gave **3** and the *tert*-carbinol (**4**) in 13 and 36% yield, respectively. The isocarbostyril (3) was identified with an authentic sample[4] by comparisons of the infrared (IR) spectrum and melting point. The structure of **4** was confirmed on the basis of the PMR spectrum showing a one-proton doublet (J 1.5 Hz)[7] due to the 1-H at δ 4.29 and two three-protons singlets due to the Me of the $C(OH)Me_2$ group newly introduced at δ 1.08 and 1.04. Photolysis of **1** in benzene gave **3** and the dimer (**5**) in 14 and 25% yield, respectively. The PMR signals for the corresponding protons in each moieties of **5** are the same, indicating **5** to be the *meso* form. Comparison of the PMR spectrum of **1** and **5** provides that the 1-, 8-H and 2-Me group in **5** are shifted upfield by 0.27, $>$0.30 and 0.66 ppm, respectively. On examination of the Dreiding model (**5a**) of **5**, it can be easily seen that the 1- and 8-H lie in the shielding zone of benzene ring of the dimethoxyphenylacetyl group in the other moiety and

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[1] Part III: M. Onda, R. Matsui, and Y. Sugama, *Chem. Pharm. Bull.* (Tokyo), **25**, 2359 (1977).
[2] Location: *Minato-ku, Tokyo 108, Japan.*
[3] M. Onda, K. Yuasa, and J. Okada, *Chem. Pharm. Bull.* (Tokyo), **22**, 2365 (1974); I. Ninomiya, O. Yamamoto, and T. Naito, *Heterocycles*, **5**, 67 (1976); *idem*, *J. Chem. Soc., Chem. Commun.*, **1976**, 437.
[4] M. Sainsbury, S.F. Dyke, and A.R. Marshall, *Tetrahedron*, **22**, 2445 (1966).
[5] M. Onda, Y. Harigaya, and T. Suzuki, *Heterocycles*, **4**, 1669 (1976).
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[7] $J_{1,3}$ 1.5 Hz.

the 2-Me group lies in the shielding zone of benzene ring of the dihydroisoquinoline group in the other moiety. This explains the PMR data observed above. Conclusively, the results obtained above lead us to that since the hydrogen atom of the 1-position in **1** is readily abstracted to give the 1-substituted compounds, this position should be protected by appropriate groups.

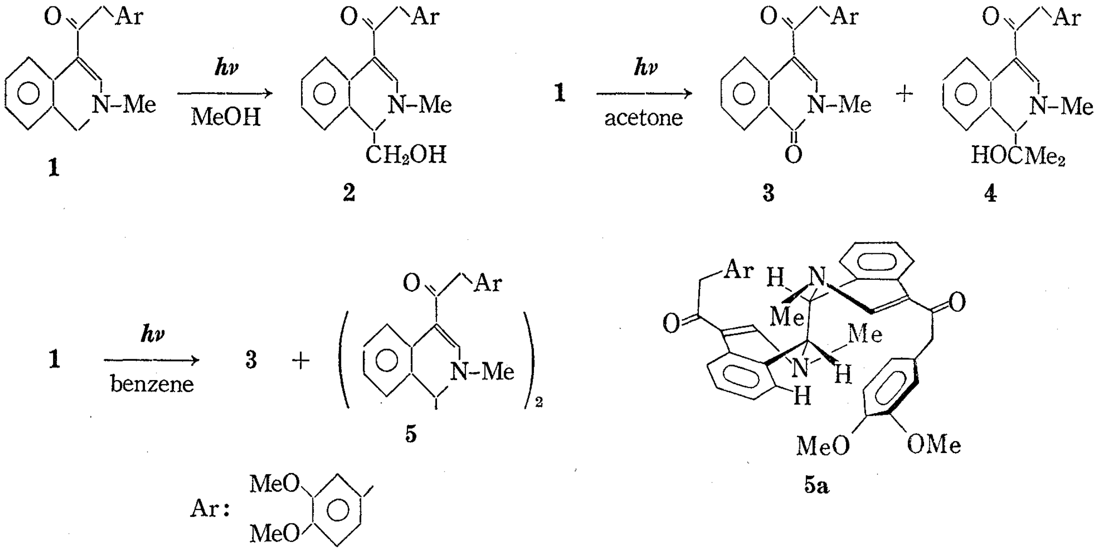

Chart 1

The isocarbostyril (**3**) is considered to be available for the above aim. Photolysis of **3** in methanol afforded the C-nor-benzo[*c*]phenanthridine (**6**) in 10% yield. The only carbonyl band observed at 1649 cm^{-1} in its IR spectrum (CCl_4) corresponds to that of the lactam group. The PMR spectrum of **6** indicates the characteristic signals for the 4-H at δ 6.92 (s), the 1-H at δ 6.76 (s), the 4b-H at δ 4.88 (d, *J* 6 Hz), the 10b-H at δ 3.81 (m), the 11-H at δ 3.17 (d, *J* 6 Hz). On the basis of these data and molecular formula, the C ring in **6** is thought to be a five-membered one, whose *cis* B/C ring fusion would be assigned from the coupling constant of the 4b-H.[8] Formation of **6** is deduced to arise from photocyclization of **3** accompanied with successive decarbonylation.[9]

We, next, planned to examine photolyses of the enol acetates (**7**) and (**8**) obtained from **3**. On acetylation with acetic anhydride in the presence of potassium acetate, **3** gave **7** and **8** in 70 and 15% yield, respectively. The PMR spectrum of **7** shows the signals for the 3-H at δ 7.39 (s), the vinyl-H at δ 6.29 (s), the 2′-H at δ 7.12 (d, *J* 2 Hz), 6′-H at δ 7.06 (q, *J* 9 and 2 Hz). That of **8** exhibits the signals for the corresponding protons at δ 7.29 (s), 6.50 (s) and 6.64—6.61 (m). On saturation of the vinyl-H in **7**, the nuclear Overhauser effect (NOE) enhancements of 12.2, 6.4, 5.9 and 5.9% for the 3-, 5-, 2′- and 6′-H, respectively, are observed. Saturation of the Me (δ 2.19) of the OAc group in **7** increases the signal intensities for the 2′- and 6′-H by 14.8%. On the other hand, saturation of the vinyl-H in **8** gives no effect on the signal intensities for the 3- and 5-H. Considering **7** and **8** to be the Z- and E-isomer, respectively, these NOE results can be understood. In the case of the E-isomer, two rings would loose coplanarity by the steric interaction. This is responsible for the upfield shifts of the 3-, 2′- and 6′-H in **8** compared to those in **7**. The downfield shift of the vinyl-H in **8** is ascribed to the anisotropic effect of the OAc group.

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8) I. Ninomiya, T. Naito, T. Kiguchi, and T. Mori, *J. Chem. Soc., Perkin I*, **1973**, 1696; I. Ninomiya, T. Naito, H. Ishii, T. Ishida, M. Ueda, and K. Harada, *ibid.*, **1975**, 762; I. Ninomiya, T. Kiguchi, O. Yamamoto, and T. Naito, *Heterocycles*, **4**, 467 (1976).

9) D.C. Necker, "Mechanistic Organic Photochemistry," Reinhold Publishing Corporation, New York, 1967, p. 53.

Photolysis of **7** in benzene gave **8** and the acetylene (**9**) in 63 and 4% yield, respectively. The PMR spectrum of **9** shows no signals for the vinyl-H and OAc group existed in that of **7**. On the other hand, the carbon nuclear magnetic resonance (^{13}C NMR) spectrum provides the signals for the acetylenic carbons at δ 92.8 and 82.1. These spectral data support the structure of **9**.

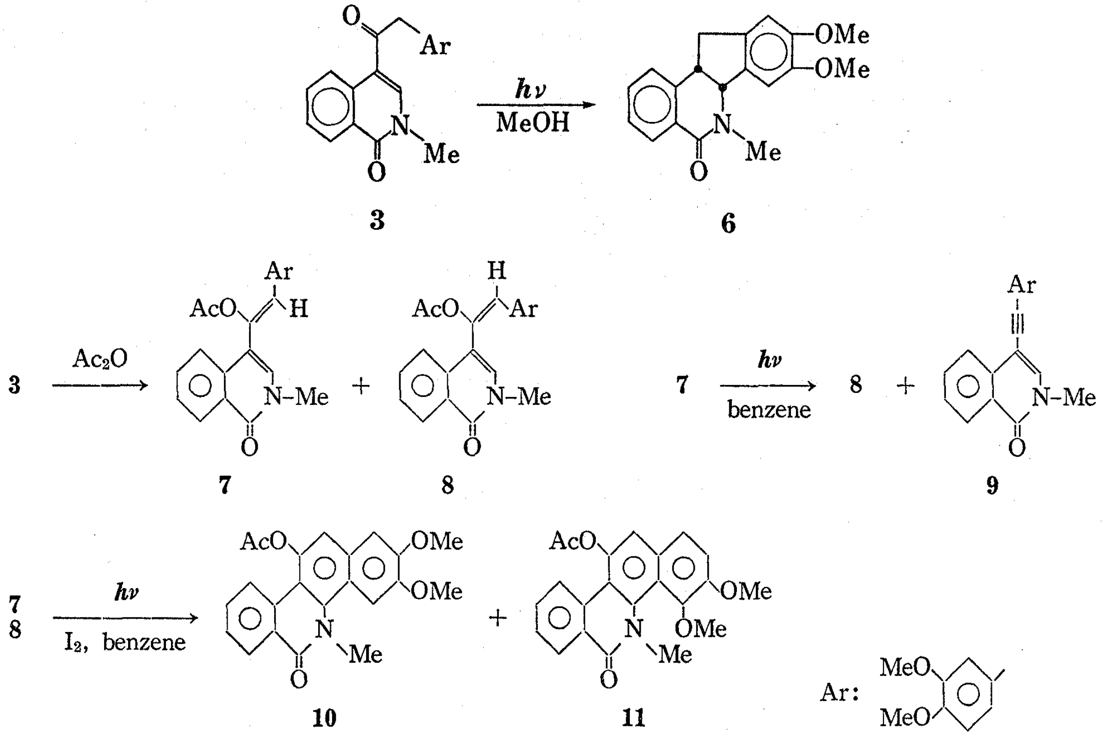

Chart 2

TABLE I. ^{13}C NMR Data of **7**, **8** and **9** (δ)

Isoquinoline group

	C-1	C-3	C-4	C-4a	C-5	C-6	C-7	C-8	C-8a	2-Me
7	162.11	133.96	114.49	135.48	124.20	132.21	126.99	128.02	125.53	37.19
8	162.11	135.48	111.76	135.48	124.32	132.57	127.22	128.08	125.71	37.25
9	162.00	136.27	101.32	136.27	124.80	132.38	127.41	127.77	125.35	37.19

Phenyl group

	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	OMe
7	126.74	111.15	148.89	148.77	111.51	120.92	55.82
8	126.02	110.91	148.59	148.46	111.03	121.71	55.76, 55.27
9	115.22	114.12	149.62	148.71	111.09	124.80	55.94

Unsaturated bond

	α	β	CO	Me
7	142.21	121.71	168.55	21.17
8	141.31	124.32	169.82	21.11
9	92.83	82.10		

Photocyclizations of the stilbenes have been well known.[10] Photolysis of **7** in benzene in the presence of iodine afforded, expectedly, the 11-acetoxybenzo[*c*]phenanthridines (**10**) and (**11**) in 27 and 18% yield, respectively. Their structures can be distinguished on the basis of the PMR data. Two aromatic protons of the D ring in **10** appear at δ 7.49 and 7.09 as singlet and those in **11** appear at δ 7.56 and δ 7.35 as doublet (J 9 Hz). The upfield shifts of the 4-OMe (0.25 ppm) and 5-Me group (0.47 ppm) in **11** compared to those in **10** may be explained as being due to their spatial orientation which arises to be free from their sterically mutual interactions. Photolysis of **8** under the same conditions as mentioned above afforded **10** and **11** in 24 and 18% yield, respectively.

Hydrolysis of **10** with methanolic potassium hydroxide quantitatively gave the phenol (**12**). On oxidation with lead tetraacetate, **12** afforded the quinone (**13**) and diacetate (**14**) in 50 and 11% yield, respectively. The diacetate (**14**) was hydrolyzed to give **13**. The quinone (**13**) shows the IR bands due to the carbonyls of the quinone and lactam groups at 1698 and 1648 cm^{-1}, respectively. The diacetate (**14**) exhibits the IR bands at 1763 (OAc) and 1648 cm^{-1} (C=O of enone and lactam), and the PMR signal for two OAc groups at δ 2.14 as singlet.

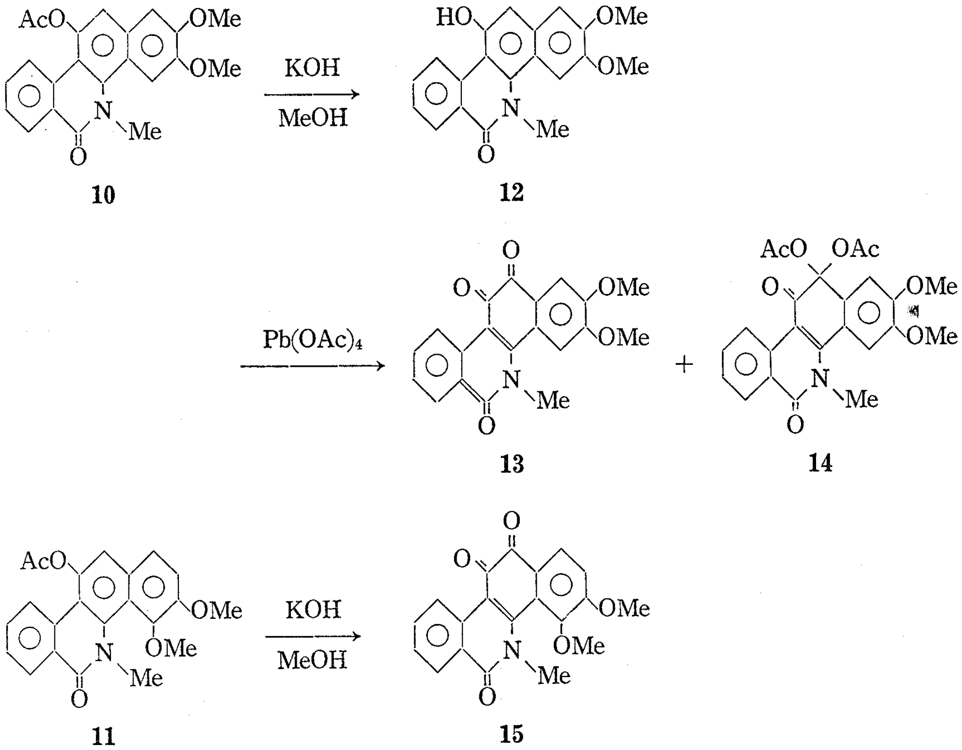

Chart 3

Hydrolysis of **11** with methanolic potassium hydroxide gave the quinone (**15**) in 19% yield, whose IR spectrum showed the carbonyl bands of the quinone and lactam groups at 1695 and 1645 cm^{-1}, respectively. Formation of **15** is thought to arise from air-oxidation of the 11-hydroxy compound obtained initially.

Attempts to obtain the analogue of chelidonine from derivative of **13** are in progress by the other group.[11]

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10) F.R. Stermitz, "Organic Photochemistry," Vol. 1, ed. by O.L. Chapman, Marcel Dekker, Inc., New York, 1967, p. 247; E.V. Blackburn and C.J. Timmons, *Quart. Rev.*, 23, 482 (1969).

11) I. Ninomiya, O. Yamamoto, and T. Naito, Abstracts of the 9th Congress of Heterocyclic Chemistry, Fukuoka, Japan, 1976, p. 131.

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Experimental

Melting points were determined on a micro hot-stage and are not corrected. IR spectra were recorded on a JASCO IR-G in a chloroform solution unless otherwise stated. PMR spectra were taken on a Varian T-60 (60 MHz) and a JEOL JNM PS-100 (100 MHz) in a deuterochloroform solution unless otherwise stated. ^{13}C NMR spectra were measured with a JEOL JNM PS-100 (25.1 MHz) in a deuterochloroform solution. Mass spectra (MS) were taken on a JEOL JMS-01S. Photolyses were carried out with a 100 W medium pressure mercury lamp under nitrogen at room temperature.

1,2-Dihydro-4-(3′,4′-dimethoxyphenylacetyl)-2-methylisoquinoline (**1**) **and 4-(3′,4′-Dimethoxyphenylacetyl)-2-methylisocarbostyril** (**3**)——These compounds were prepared by the procedures described in the literature.[4]

The 1,2-Dihydroisoquinoline (**1**): Colorless prisms, mp 111—118° (from ethanol). IR ν_{max} cm^{-1}: 1620, 1600 (N–C=C–C=O). PMR (60 MHz) δ: 8.84 (1H, q, J 8 and 2 Hz, 5-H), 7.40 (1H, s, 3-H), 7.12—6.82 (3H, m, 6-, 7- and 8-H), 6.79 (3H, s, 2′-, 5′- and 6′-H), 4.40 (2H, s, 1-H_2), 3.86 (8H, s, 7′-H_2 and 2×OMe), 3.00 (3H, s, 2-Me).

The Isocarbostyril (**3**): Colorless needles, mp 167—168° (from ethanol). IR ν_{max} cm^{-1}: 1647 (N–C=O). PMR (60 MHz) δ: 8.79 (1H, q, J 8 and 2 Hz, 5-H), 8.42 (1H, q, J 8 and 2 Hz, 8-H), 8.00 (1H, s, 3-H), 7.71 (1H, dt, J 8 and 2 Hz, 6-H), 7.48 (1H, dt, J 8 and 2 Hz, 7-H), 6.81 (3H, s, 2′-, 5′- and 6′-H), 4.11 (2H, s, 7′-H_2), 3.86 (6H, s, 2×OMe), 3.64 (3H, s, 2-Me).

Photolyses of 1——a) A solution of **1** (100 mg) and BF_3-etherate (54 mg) in methanol (150 ml) was irradiated for 3 hr. After removal of solvent *in vacuo*, the remaining residue was dissolved in ethyl acetate. The resulting solution was washed with 10% aq. Na_2CO_3 and a saturated aq. NaCl, and then dried over Na_2SO_4. Work-up gave an oil (100 mg) which was purified by pre. TLC[12] (silica gel plates; benzene–ethyl acetate=1:2, v/v). The zone with Rf 0.15 gave 1,2-dihydro-1-hydroxymethyl-4-(3′,4′-dimethoxyphenylacetyl)-2-methylisoquinoline (**2**) (52 mg, 48%) as oil. IR ν_{max} cm^{-1}: 3600, 3450 (OH), 1620, 1590 (N–C=C–C=O). PMR (100 MHz) δ: 8.60 (1H, q, J 7 and 2 Hz, 5-H), 7.51 (1H, d, J 1.5 Hz, 3-H), 7.30—6.68 (3H, m, 6-, 7- and 8-H), 6.80 –6.76 (3H, m, 2′-, 5′- and 6′-H), 4.44 (1H, sex, J 5 and 1.5 Hz, 1-H), 3.86 (2H, s, 7′-H_2), 3.82 (6H, s, 2×OMe), 3.69 (1H, q, J 11 and 5 Hz, $C\underline{H}_AOH$), 3.58 (1H, q, J 11 and 5 Hz, $C\underline{H}_BOH$), 3.26 (3H, s, 2-Me), 2.17 (1H, s, OH).[13] MS m/e: M^+, 353.1647. Calcd. for $C_{21}H_{23}NO_4$: M, 353.1627.

b) A solution of **1** (100 mg) in acetone (200 ml) was irradiated for 15 min. Work-up afforded an oil (140 mg) which was purified by pre. TLC (silica gel plates; benzene–ethyl acetate=1:1, v/v). The zone with Rf 0.45 gave **3** (14 mg, 13%) as colorless prisms of mp 165—167° (from ethanol). The zone with Rf 0.24 gave an oil (55 mg) which was further purified by pre. TLC (alumina plates; benzene–ethyl acetate=1:1, v/v) to provide 1,2-dihydro-1-(β-hydroxyisopropyl)-4-(3′,4′-dimethoxyphenylacetyl)-2-methylisoquinoline (**4**) (42 mg, 36%) as colorless prisms of mp 190—192° (from ethanol–ether) from the zone with Rf 0.47. IR ν_{max} cm^{-1}: 3600, 3450 (OH), 1620, 1592 (N–C=C–C=O). PMR (100 MHz) δ: 8.66 (1H, q, J 8 and 2 Hz, 5-H), 7.60 (1H, d, J 1.5 Hz, 3-H), 7.40—6.86 (3H, m, 6-, 7- and 8-H), 6.80—6.78 (3H, m, 2′-, 5′- and 6′-H), 4.29 (1H, d, J 1.5 Hz, 1-H), 3.89 (2H, s, 7′-H_2), 3.82 (6H, s, 2×OMe), 3.34 (3H, s, 2-Me), 1.67 (1H, s, OH),[13] 1.08 (3H, s, Me), 1.04 (3H, s, Me). MS m/e: M^+, 381.1928. Calcd. for $C_{23}H_{27}NO_4$: M, 381.1940.

c) A solution of **1** (100 mg) in benzene (200 ml) was irradiated for 4 hr. On removal of solvent *in vacuo*, an oil (110 mg) was obtained. Its pre. TLC (silica gel plates; benzene–ethyl acetate=1:1, v/v) afforded **3** (15 mg, 14%) as colorless prisms of mp 168—169° (from ethanol) from the zone with Rf 0.45. The zone with Rf 0.38 gave 1,1′,2,2′-tetrahydro-2,2′-dimethyl-4,4′-bis(3″,4″-dimethoxyphenylacetyl)-1,1′-biisoquinolyl (**5**) (25 mg, 25%) as colorless prisms of mp 224—225° (from ethanol). IR ν^{KBr}_{max} cm^{-1}: 1621, 1584 (N–C=C–C=O). PMR (100 MHz) δ[14]: 8.62 (1H, q, J 8 and 1.5 Hz, 5-H), 7.49 (1H, s, 3-H), 7.42—7.06 (2H, m, 6- and 7-H), 6.89—6.87 (3H, m, 2″-, 5″- and 6″-H), 6.51 (1H, q, J 8 and 2 Hz, 8-H), 4.13 (1H, s, 1-H), 3.99 (2H, s, 7″-H_2), 3.86 (3H, s, OMe), 3.85 (3H, s, OMe), 2.34 (3H, s, 2-Me). MS m/e: M^+, 644.2915. Calcd. for $C_{40}H_{40}N_2O_6$: M, 644.2886.

Photolysis of 3——A solution of **3** (120 mg) in methanol (150 ml) was irradiated for 4 hr. Work-up gave an oil (105 mg) whose pre. TLC (alumina plates; benzene–ethyl acetate=3:1, v/v) provided C-nor-4b,5,6,10b,-11-pentahydro-5-methyl-6-oxobenzo[*c*]phenanthridine (**6**) (11 mg, 10%) as colorless needles of mp 162—162.5° (from benzene–ether) from the zone with Rf 0.31. IR $\nu^{CCl_4}_{max}$ cm^{-1}: 1649 (N–C=O). PMR (100 MHz) δ: 8.15 (1H, q, J 8 and 2 Hz, 7-H), 7.56—7.22 (3H, m, 8-, 9- and 10-H), 6.92 (1H, s, 4-H), 6.76 (1H, s, 1-H), 4.88 (1H, d, J 6 Hz, 4b-H), 3.87 (3H, s, OMe), 3.84 (3H, s, OMe), 3.81 (1H, m, 10b-H), 3.17 (3H, s, 5-Me), 3.17 (2H, d, J 6 Hz, 11-H_2). MS m/e: M^+, 309.1359. Calcd. for $C_{19}H_{19}NO_3$: M, 309.1364.

Acetylation of 3——A mixture of **3** (500 mg), potassium acetate (300 mg) and acetic anhydride (20 ml) was refluxed for 5 hr. After evaporation *in vacuo*, the remaining residue was dissolved in ethyl acetate. The resulting solution was washed with a saturated aq. NaCl and dried over Na_2SO_4. Work-up gave an oil (600

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12) Preparative thin-layer chromatography.

13) On addition of D_2O, this signal disappeared.

14) The corresponding protons in each moieties respectively show the same chemical shifts.

mg). Its pre. TLC (silica gel plates; benzene–ethyl acetate=1: 1, v/v) gave (Z)-4-(α-acetoxy-3′,4′-dimethoxystyryl)-2-methylisocarbostyril (**7**) (370 mg, 70%) and the E-isomer (**8**) (78 mg, 15%) from the zones *Rf* 0.46 and 0.58, respectively. The Z-isomer (**7**): colorless prisms, mp 173—174° (from ethanol). IR $\nu_{\max}$ cm^{-1}: 1758 (OAc), 1645 (N–C=O). PMR (100 MHz) δ: 8.48 (1H, q, *J* 8 and 2 Hz, 8-H), 7.88 (1H, q, *J* 8 and 2 Hz, 5-H), 7.68 (1H, dt, *J* 8 and 2 Hz, 6-H), 7.48 (1H, dt, *J* 8 and 2 Hz, 7-H), 7.39 (1H, s, 3-H), 7.12 (1H, d, *J* 2 Hz, 2′-H), 7.06 (1H, q, *J* 9 and 2 Hz, 6′-H), 6.88 (1H, d, *J* 9 Hz, 5′-H), 6.29 (1H, s, vinyl-H), 3.88 (6H, s, 2×OMe), 3.61 (3H, s, 2-Me), 2.19 (3H, s, OAc). MS *m/e*: M+, 379.1408. Calcd. for $C_{22}H_{21}NO_5$: M, 379.1419. The E-isomer (**8**): colorless prisms, mp 148.5—149.5° (from ethanol). IR $\nu_{\max}$ cm^{-1}: 1753 (OAc), 1645 (N–C=O). PMR (100 MHz) δ: 8.47 (1H, q, *J* 8 and 2 Hz, 8-H), 7.79—7.41 (3H, m, 5-, 6- and 7-H), 7.29 (1H, s, 3-H), 6.64—6.61 (3H, m, 2′-, 5′- and 6′-H), 6.50 (1H, s, vinyl-H), 3.77 (3H, s, OMe), 3.54 (3H, s, OMe), 3.36 (3H, s, 2-Me), 2.13 (3H, s, OAc). MS *m/e*: M+, 379.1446. Calcd. for $C_{22}H_{21}NO_5$: M, 379.1419.

Photolyses of 7——a) A solution of **7** (190 mg) in benzene (160 ml) was irradiated for 30 min. Work-up afforded an oil (185 mg) which was purified by pre. TLC (silica gel plates; benzene–ethyl acetate=1: 1, v/v). From the zone with *Rf* 0.46, **7** (27 mg, 14%) was recovered. The zone with *Rf* 0.53 gave **8** (120 mg, 63%). The zone with *Rf* 0.62 afforded 4-(3′,4′-dimethoxyphenylethynyl)-2-methylisocarbostyril (**9**) (6 mg, 4%) as colorless prisms of mp 156—157° (from benzene–hexane). IR $\nu_{\max}$ cm^{-1}: 1646 (N–C=O). PMR (100 MHz) δ: 8.45 (1H, q, *J* 8 and 2 Hz, 8-H), 8.02 (1H, q, *J* 8 and 2 Hz, 5-H), 7.72 (1H, dt, *J* 8 and 2 Hz, 6-H), 7.51 (1H, dt, *J* 8 and 2 Hz, 7-H), 7.45 (1H, s, 3-H), 7.16 (1H, q, *J* 8 and 2 Hz, 6′-H), 7.05 (1H, d, *J* 2 Hz, 2′-H), 6.85 (1H, d, *J* 8 Hz, 5′-H), 3.90 (6H, s, 2×OMe), 3.60 (3H, s, 2-Me). MS *m/e*: M+, 319.1231. Calcd. for $C_{20}H_{17}NO_3$: M, 319.1208.

b) A solution of **7** (100 mg) in benzene (140 ml) was irradiated in the presence of I_2 (3.4 mg) for 30 min. Work-up afforded an oil (114 mg) which was purified by pre. TLC (silica gel plates; benzene–ethyl acetate=1: 1, v/v) to give 11-acetoxy-5,6-dihydro-2,3-dimethoxy-5-methyl-6-oxobenzo[*c*]phenanthridine (**10**) (27 mg, 27%) and 3,4-dimethoxy-isomer (**11**) (18 mg, 18%) from the zones with *Rf* 0.33 and 0.46, respectively.

The 2,3-Dimethoxy-isomer (**10**): Colorless needles, mp 208.5—210° (from ethanol). IR $\nu_{\max}$ cm^{-1}: 1763 (OAc), 1640 (N–C=O). PMR (100 MHz) δ: 8.70 (1H, q, *J* 8 and 2 Hz, 7-H), 8.61 (1H, q, *J* 8 and 2 Hz, 10-H), 7.72 (1H, dt, *J* 8 and 2 Hz, 9-H), 7.56 (1H, dt, *J* 8 and 2 Hz, 8-H), 7.49 (1H, s, 4-H), 7.30 (1H, s, 12-H), 7.09 (1H, s, 1-H), 4.00 (6H, s, 2×OMe), 3.97 (3H, s, 5-Me), 2.49 (3H, s, OAc). MS *m/e*: M+, 377.1258. Calcd. for $C_{22}H_{19}NO_5$: M, 377.1263.

The 3,4-Dimethoxy-isomer (**11**): Colorless prisms, mp 171—171.5° (from ethanol). IR $\nu_{\max}$ cm^{-1}: 1763 (OAc), 1639 (N–C=O). PMR (100 MHz) δ: 8.64 (1H, q, *J* 8 and 2 Hz, 7-H), 8.62 (1H, q, *J* 7 and 2 Hz, 10-H), 7.75 (1H, dt, *J* 7 and 2 Hz, 9-H), 7.67 (1H, dt, *J* 7 and 2 Hz, 8-H), 7.56 (1H, d, *J* 9 Hz, 1-H), 7.35 (1H, d, *J* 9 Hz, 2-H), 7.29 (1H, s, 12-H), 4.00 (3H, s, 3-OMe), 3.75 (3H, s, 4-OMe), 3.50 (3H, s, 5-Me), 2.47 (3H, s, OAc). MS *m/e*; M+, 377.1241. Calcd. for $C_{22}H_{19}NO_5$: M, 377.1263.

Photolysis of 8——A solution of **8** (94 mg) in benzene (140 ml) was irradiated in the presence of I_2 (3 mg) for 25 min. Work-up gave **10** (23 mg, 24%) and **11** (16 mg, 18%).

5,6-Dihydro-11-hydroxy-2,3-dimethoxy-5-methylbenzo[*c*]phenanthridine (12)——To a solution of KOH (84 mg) in methanol (60 ml) was added **10** (112 mg) and the reaction mixture was stirred for 16 hr at room temperature. After removal of solvent *in vacuo*, the resulting residue was extracted with chloroform to give **12** (96 mg, 96%) as light violet crystals of mp 269—271°. IR $\nu_{\max}$ cm^{-1}: 3600 (OH), 1638 (N–C=O). PMR (100 MHz) (DMSO-d_6)[15] δ: 10.52 (1H, s, OH),[13] 9.39 (1H, q, *J* 8 and 2 Hz, 10-H), 8.36 (1H, q, *J* 8 and 2 Hz, 7-H), 7.78 (1H, dt, *J* 8 and 2 Hz, 9-H), 7.53 (1H, dt, *J* 8 and 2 Hz, 8-H), 7.44 (1H, s, 4-H), 7.11 (1H, s, 12-H), 7.08 (1H, s, 1-H), 3.89 (6H, s, 2×OMe), 3.85 (3H, s, 5-Me). MS *m/e*: M+, 335.1158. Calcd. for $C_{20}H_{17}NO_4$: M, 335.1170.

Oxidation of 12——A mixture of **12** (45 mg), lead tetraacetate (150 mg), acetic anhydride (1.5 ml) and acetic acid (1.5 ml) was stirred for 5.5 hr at 67°. After addition of H_2O and removal of solvent *in vacuo*, the resulting residue was extracted with chloroform to give a brown solid (55 mg) which was washed with ether to afford 5,6,11,12-tetrahydro-2,3-dimethoxy-5-methyl-6,11,12-trioxobenzo[*c*]phenanthridine (**13**) (30 mg, 50%) as violet crystals of mp>300°. MS *m/e*: M+, 349.0957. Calcd. for $C_{20}H_{15}NO_5$: M, 349.0950. From the ethereal solution, 12,12-diacetoxy-5,6,11,12-tetrahydro-2,3-dimethoxy-5-methyl-6,11-dioxobenzo[*c*]phenanthridine (**14**) (7 mg, 11%) was obtained as yellow crystals of mp>300° (from ethanol). PMR (100 MHz) δ: 8.96 (1H, q, *J* 8 and 2 Hz, 10-H), 8.42 (1H, q, *J* 8 and 2 Hz, 7-H), 7.73 (1H, dt, *J* 8 and 2 Hz, 9-H), 7.50 (1H, dt, *J* 8 and 2 Hz, 8-H), 7.30 (1H, s, 4-H), 7.08 (1H, s, 1-H), 3.95 (3H, s, OMe), 3.91 (3H, s, OMe), 3.86 (3H, s, 5-Me), 2.14 (6H, s, 2×OAc). MS *m/e*: M+, 451.1281. Calcd. for $C_{24}H_{21}NO_8$: M, 451.1267.

Hydrolysis of 14——To a solution of KOH (49 mg) in methanol (25 ml) was added **14** (40 mg) and the reaction mixture was stirred for 3 days at room temperature. After removal of solvent *in vacuo*, the resulting residue was extracted with chloroform. Work-up gave a brown solid (25 mg) which was washed with ether to give **13** (10 mg, 32%).

Hydrolysis of 11——To a solution of KOH (60 mg) in methanol (3 ml) was added **11** (80 mg) and the reaction mixture was stirred for 4 hr at room temperature. After removal of solvent *in vacuo*, the resulting

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[15] Dimethyl sulfoxide-d_6.

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residue was extracted with chloroform. Work-up gave an oil (40 mg) which was purified by pre. TLC (silica gel plates; benzene–ethyl acetate=1: 1, v/v) to give 5,6,11,12-tetrahydro-3,4-dimethoxy-5-methyl-6,11,12-trioxobenzo[*c*]phenanthridine (**15**) (14 mg, 19%) as red crystals of mp 238—244° (from methanol). PMR (100 MHz) δ: 9.21 (1H, q, *J* 8 and 2 Hz, 10-H), 8.46 (1H, q, *J* 8 and 2 Hz, 7-H), 7.84 (1H, d, *J* 8 Hz, 1-H), 7.72 (1H, dt, *J* 8 and 2 Hz, 9-H), 7.58 (1H, dt, *J* 8 and 2 Hz, 8-H), 7.06 (1H, d, *J* 8 Hz, 2-H), 4.01 (3H, s, 3-OMe), 3.66 (6H, s, 4-OMe and 5-Me). MS *m/e*: M^+, 349.0993. Calcd. for $C_{20}H_{15}NO_5$: M, 349.0950.