Site-Selective Diels−Alder Reactions of 7-(Methoxyimino)-4-methylchromene-2,8-dione with Alkenes

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Regio- and site-selective Diels−Alder reactions of *o*-quinone monooxime **1** are reported. The electron rich dienophiles **2**, **4**, **6**, **8**, and **10** react with the exocyclic diene system of monooxime **1** leading to the coumarin derivatives **3**, **5**, **7**, **9**, **11**, and **12**. The electron deficient dienophiles **13a,b** and **18** react with the quinoid and the pyrone diene systems of compound **1** affording the cycloadducts **14a,b**, **17a,b**, and **19**.

1,4-Cycloaddition reactions of alkenes with *o*-quinone monoimides are well known.[1] A few similar reactions of alkenes with *o*-quinone monooximes, leading to the formation of 2*H*-1,4-oxazines, through dehydration of the initially formed 1,4-cycloaddition products, have also been reported.[2] Attempted reaction of *O*-methyl ethers of some *o*-quinone monooximes with DMAD failed to produce oxazines even after prolonged reaction times.[3] In a former paper we reported that 10-(methoxyimino)-phenanthren-9-one reacts with this dienophile to give dimethyl 7-oxo-7*H*-dibenzo[*de*,*g*]quinoline-4,5-dicarboxylate *via* an unusual [4 + 2] cycloaddition of the dienophile across the heterodiene system (C═C−C═N−OCH_3), which incorporates an aromatic C−C bond.[4] Very recently we reported[5] Diels−Alder reactions of *trans*-stilbene with the exocyclic heterodiene system of monooxime *O*-methyl ethers of phenanthrene-9,10-quinone, [4,7]phenanthroline-5,6-dione, and 4,6-di-*tert*-butyl-*o*-benzoquinone leading to the formation of 2*H*-1,4-benzoxazines along with benzoxazole derivatives. Furthermore, Diels−Alder cycloadditions of 2-pyrones with alkenes are known[6] to form benzene derivatives through CO_2 abstraction and subsequent aromatization.

We report herein our studies on the reaction of several dienophiles with 7-(methoxyimino)-4-methylchromene-2,8-dione (**1**). The investigation was stimulated by the potential chemoselectivity in Diels−Alder cycloaddition to its three diene systems, the external O═C−C═N, the *o*-quinoid array found at carbons 6,5,4a,8a, and the pyranone framework located at carbons 3,4,4a,8a (Schemes 1, 2).

Treatment of monooxime **1** with *trans*-stilbene (**2**) for 7 d in refluxing chloroform gave compound **3** in 62% yield, along with some unreacted starting oxime (27%). The analytical and spectral data of this compound are in good agreement with the proposed structure **3**. Its ^{1}H NMR spectrum showed a singlet at δ 6.17 (1H), two doublets at δ 4.40 (1H) and 5.46 (1H), and a multiplet at δ 7.07−7.23 for 12 aromatic protons, while the ^{13}C NMR spectrum exhibited absorptions for four aliphatic carbon atoms at δ 18.8 (7-CH_3), 63.4 (CH_3O), 68.2 (C-3), and 82.8 (C-2), a fact revealing that the 1,4-cycloaddition of **2** proceeds at the external 1,4-oxaza-1,3-diene system of **1**.

Treatment of compound **1** with excess α-methylstyrene (**4**) for 2 h under reflux gave the 2-methyl-2-phenyl-oxazine derivative **5**, similar to **3** in 57% yield.

When compound **1** was reacted with excess vinyl acetate (**6**) under reflux for 4 d, product **7** (32%) was also obtained,[7] along with the unreacted starting oxime **1** (38%). No efforts were made to optimize the yield.

The reaction of **1** with excess butyl vinyl ether (**8**) for 2.5 d under reflux gave compound **9** (18%), while the reaction of monooxime **1** with excess 3,4-dihydro-2*H*-pyran (**10**) for 24 h gave the regioisomers **11** (55%) and **12** (6%).

The structures for adducts **5**, **9**, **11**, **12** were established on the basis of their spectral properties, in comparison with those of compounds **3**, **7** as well as of other similar derivatives of 2,3-dihydro-4*H*-1,4-benzoxazines.[1a] The ^{13}C NMR signals for the C-2 carbons of **3** and **5** are at δ 82.8 and 80.2, respectively, while the chemical shifts for the same carbon atoms in **7**, **9**, and **11** are 89.7, 96.9, and 94.8, respectively. The ^{13}C NMR chemical shifts for the carbon C-3, adjacent to the nitrogen atom, in **5**, **7**, **9,** and **11** are 56.4, 50.6, 52.0, and 54.8, respectively. Compound **12** shows ^{13}C NMR signals for C-7a, C-11a, and C-9 (Scheme 1) at 81.9, 72.2, and 67.4, respectively. Furthermore the proton signals for *N*-methoxy, 7-methyl, and 8-H protons of the benzopyranooxazine skeleton in **3**, **5**, **7**, **9**, **11**, **12** are at δ 3.51−3.85, 2.36−2.42, and 6.14−6.17, respectively, being very similar to each other.

† X-ray structural analysis.

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(7) The structure of **7** was unequivocally established by X-ray crystallographic analysis (supporting information).

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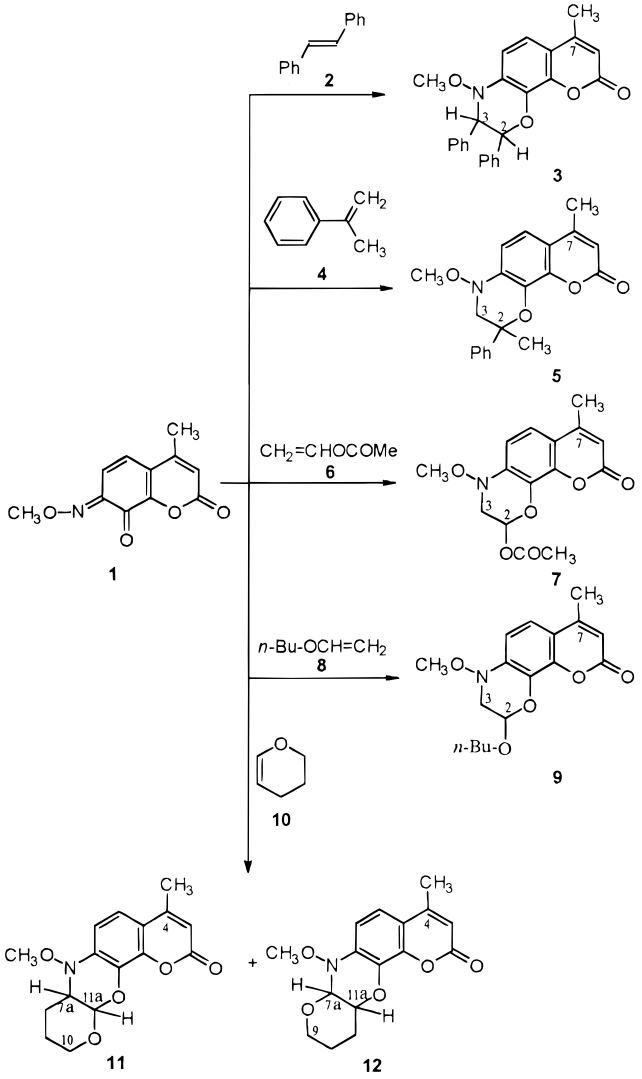
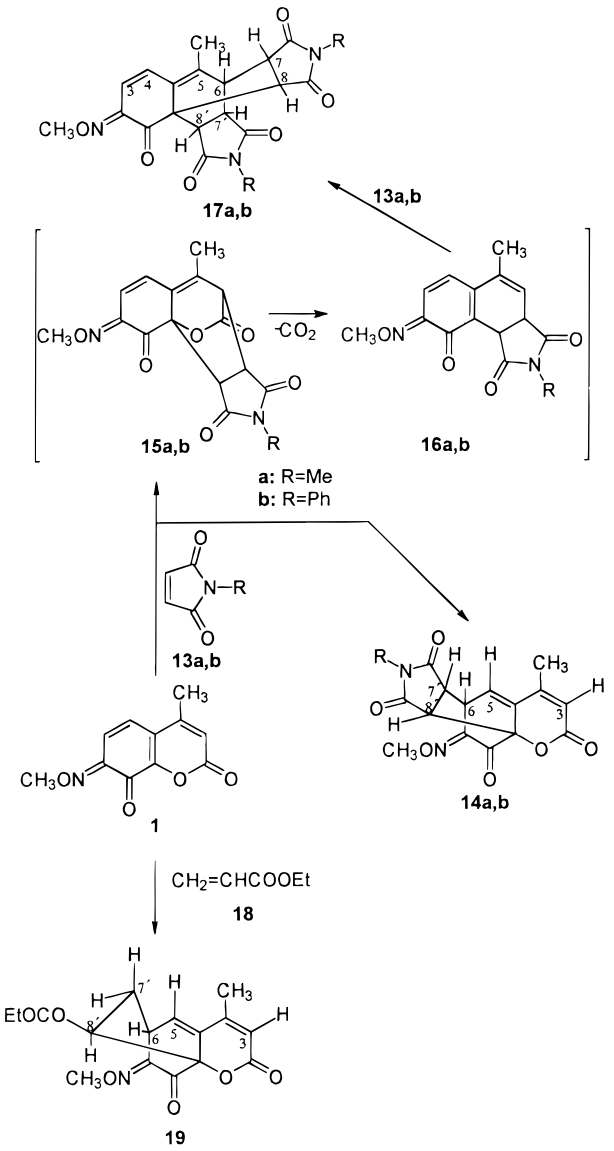
Scheme 1



Scheme 2



Moreover in the ^{1}H NMR spectrum of **11** signals for the H-11a and H-7a (Scheme 1) are observed at δ 5.61 (d, 1H, J = 2.5 Hz) and 3.71 (ddd, 1H, J = 2.5, 4.2, 10.3 Hz) with coupling constants indicating equatorial and axial position, respectively. In the ^{1}H NMR spectrum of **12** the protons H-11a and H-7a resonate at δ 4.56 (t, 1H, J = 3.0 Hz) and 4.86 (s, 1H), respectively, in agreement with the proposed structures for these two regioisomers. Due to the low values of the coupling constants (one of them seems to be almost zero), and in relation to the structure of product **11**, equatorial and axial positions are assumed for the protons H-11a and H-7a, respectively.

The observed regioselectivity in the reactions studied is in agreement with that reported for the cycloadditions of some electron-rich alkenes to the *N*-(2,4-dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (an *o*-quinone monoimide), which proceeds regiospecifically with the more electron-rich carbon of the dienophile adding to the nitrogen atom of the heterodiene system of imide.[1a] A number of 1- and/or 4-substituted 1,3-butadienes react with the same imide in an inverse electron-demand Diels−Alder reaction to give derivatives of 2,3-dihydro-1,4-benzoxazines, while 1,3-butadiene adds across the *N*-acylimino group of the imide to give a spiro adduct.[1d] Steric factors appear to be responsible for these results.

Refluxing **1** with excess *N*-methylmaleimide (**13a**) in chlorobenzene for 1 h afforded cycloadducts **14a** (61%) and **17a** (21%) (Scheme 2). The ^{1}H NMR spectrum of **14a** exhibits singlets at δ 1.98 (CCH_3), 2.95 (NCH_3), 4.17 (CH_3ON), and 5.97 (H-3) as well as chemical shifts at δ 3.34 (dd, 1H, J = 3.0 and 8.7 Hz, H-7′), 3.55 (d, 1H, J = 8.7, H-8′), 5.03 (dd, 1H, J = 3.0 and 6.6 Hz, H-6), and 6.43 (d, 1H, J = 6.6 Hz, H-5), thus supporting the structure proposed. Moreover the ^{13}C NMR spectrum exhibits chemical shifts at δ 146.7 and 159.6, 173.3, 174.7, 184.9 for the imine and the carbonyl carbons, respectively, and at δ 33.3, 40.2, 44.3, and 85.5 for the four ring aliphatic carbon atoms.

Structure assignment of the cycloadduct **17a** was initially based on its ^{1}H NMR spectrum, which shows singlets at δ 2.84 (6H) and 4.24 (3H) for the NCH_3 and $NOCH_3$ protons and other signals at δ 3.21 (dd, 2H, J = 2.9 and 8.4 Hz, H-7, H-7′), 3.74 (d, 2H, J = 8.4 Hz, H-8, H-8′), and 3.72 (t, 1H, J = 2.9 Hz, H-6). These data support the suggested symmetric structural form **17a**, but are not informative for the *endo* or *exo* orientation of the imide rings in the cycloadduct. This structure was unequivocally confirmed by X-ray crystallography (supporting information), which shows the *endo* orientation of both dienophile molecules during their cycloadditions,

affording a structure with C_5 symmetry somewhat reminiscent of an airplanelike framework. The ^{13}C NMR spectrum exhibits chemical shifts at δ 145.9 and 174.8, 175.7, 191.9 for the imine and the carbonyl carbons, respectively and at δ 41.0, 43.5, 48.3, and 50.1 for the four ring aliphatic carbon atoms. The *N*-methoxy protons of compound **1** also resonate[8] at δ 4.33, like those of **14a**, **17a**, obviously due to the deshielding effect caused by the resonance form $CH_3-O^+=N-C=C-O^-$ of their heterodiene system. The ^{13}C NMR signals of the imine and carbonyl carbons of **1** are at δ 151.5 and 173.8, respectively.

The main product **14a** is obviously formed *via* a site-selective Diels−Alder addition of **13a** to the 1,3-diene system of the quinoid ring of **1**, extended across the 6,5,-4a,8a-carbon atoms. On the other hand, cycloaddition of **13a** to the diene system of the pyrone across the 3,4,-4a,8a carbon atoms of **1** leads to the intermediate **15a.** Then carbon dioxide elimination, known for Diels−Alder adducts of pyrones,[9] affords intermediate **16a**. Further cycloaddition of a second molecule of **13a** to the intermediate **16a** accounts for the formation of the symmetric product **17a.**

The reaction of **1** with *N*-phenylmaleimide (**13b**) afforded compounds **14b** (51%) and **17b** (13%), analogous to those obtained from **13a**.

When compound **1** was refluxed in excess ethyl acrylate (**18**) for 6 h, compound **19** (45%) was obtained, along with a complex mixture of other products, inseparable even after repeated efforts by column chromatography or preparative TLC. The ^1H NMR spectrum of the mixture shows chemical shifts for OCH_3 protons at δ 3.80, 3.89, 4.21. A product similar to the pyrone double adduct **17** is presumed to be a component of that mixture. The ^1H NMR spectrum of **19** exhibits singlets at δ 2.08 (CCH_3), 4.10 ($NOCH_3$), and 5.90 (H-3) and other chemical shifts at δ 1.87 (ddd, 1H, J = 2.8, 6.0 and 13.2 Hz, H-7′$_{eq}$), 2.35 (ddd, 1H, J = 2.8, 10.6, and 13.2 Hz, H-7′$_{ax}$), 3.31 (dd, 1H, J = 6.0 and 10.6 Hz, H-8′), 4.53 (dt, 1H, J = 2.8 and 6.8 Hz, H-6) and 6.62 (d, 1H, J = 6.8 Hz, H-5) (Scheme 2) analogous to **14a**. Homonuclear double resonance experiments show coupling of the peak at 4.53 with the peaks at 1.87, 2.35, and 6.62, and also coupling of the peak at 3.31 with the peaks at 1.87 and 2.35. These data strongly support the suggested structure of compound **19**, obviously formed *via* a regioselective Diels−Alder addition of **18** to the 1,3-dienic system of the quinoid ring of **1**, extended across the 6,5,4a,8a-carbon atoms, analogous to **14**, with the more electron-deficient carbon atoms of the dienophile adding to the C-6.

In conclusion, electron-rich alkenes are added exclusively to the exocyclic heterodiene system of **1** showing site- and regioselectivity. The electron-deficient dienophiles reacted less selectively, mainly across the quinoid diene system, while a low yield cycloadduct was also obtained from the pyrone diene system of **1.** The easily prepared cycloadducts **3**, **5**, **7**, **9**, **11**, **12** are new coumarin derivatives with an oxazine ring angularly fused to their benzene ring and with possible biological activities, like other similar compounds.[10]

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Experimental Section

All melting points are uncorrected. IR spectra were obtained as Nujol mulls. ^1H NMR spectra were recorded with deuteriochloroform as a solvent at 300 MHz with TMS as an internal standard. ^{13}C NMR spectra were obtained at 75.5 MHz in deuteriochloroform solutions with TMS as internal reference. Mass spectra were determined with ionization energy maintained at 70 eV. 7-(Methoxyimino)-4-methylchromene-2,8-dione was prepared as described:[8] ^{13}C NMR δ 19.0, 65.6, 115.1, 120.2, 122.1, 125.5, 147.7, 148.3, 151.5, 158.3, 173.8.

4-Methoxy-7-methyl-2,3-diphenyl-2,3,4,9-tetrahydro-[1]benzopyrano[8,7-*b*][1,4]oxazin-9-one (3). A solution of 7-(methoxyimino)-4-methylchromene-2,8-dione (**1**) (219 mg, 1 mmol) and *trans*-stilbene (**2**) (200 mg, 1.1 mmol) was refluxed in $CHCl_3$ (15 mL) for 7 d. The solvent was evaporated, and the residue was chromatographed (silica gel, 1:1 *n*-hexane/CH_2Cl_2) to give **3** (210 mg, 62%): mp 197−199 °C (from *n*-hexane/CH_2Cl_2); IR 1720, 1605 cm^{-1}; ^1H NMR δ 2.42 (s, 3H), 3.51 (s, 3H), 4.40 (d, 1H, J = 8.6 Hz), 5.46 (d, 1H, J = 8.6 Hz), 6.17 (s, 1H), 7.07−7.23 (m, 12H); ^{13}C NMR δ 18.8, 63.4, 68.2, 82.8, 111.8, 112.1, 112.8, 113.1, 116.1, 116.2, 119.4, 127.5, 128.1, 128.2, 128.5, 129.0, 129.4, 135.8, 136.1, 152.6, 160.7; mass spectrum *m*/*z* (rel intensity) 399 (M^+, 4), 397 (7), 369 (31), 366 (14), 307 (100), 305 (33), 290 (27), 202 (97). Anal. Calcd for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51. Found: C, 74.88; H, 5.11; N, 3.35. Compound **1** (60 mg, 27%) was then eluted.

4-Methoxy-2,7-dimethyl-2-phenyl-2,3,4,9-tetrahydro-[1]benzopyrano[8,7-*b*][1,4]oxazin-9-one (5). A solution of compound **1** (328 mg, 1.5 mmol) in α-methylstyrene (**4**) (4 mL) was refluxed for 2 h. The excess **4** was evaporated, and the residue was chromatographed (silica gel, 1.5:1 *n*-hexane/ethyl acetate) to give compound **5** (288 mg, 57%): mp 145−147 °C (from ether); IR 1720, 1600 cm^{-1}; ^1H NMR δ 1.71 (s, 3H), 2.36 (s, 3H), 3.53 (d, 1H, J = 10.8 Hz), 3.74 (s, 3H), 3.83 (d, 1H, J = 10.8 Hz), 6.15 (s, 1H), 6.97 (d, 1H, J = 8.7 Hz), 7.06 (d, 1H, J = 8.7 Hz), 7.23−7.37 (m, 3H), 7.47 (d, 2H, J = 7.4 Hz); ^{13}C NMR δ 18.8, 27.8, 56.4, 61.3, 80.2, 110.9, 112.4, 114.9, 115.8, 122.9, 124.4, 127.5, 128.5, 130.9, 138.2, 142.9, 152.8, 161.1; mass spectrum *m*/*z* (rel intensity) 337 (M^+, 100), 322 (9), 308 (29), 307 (82), 306 (98), 305 (28), 291 (24), 204 (77), 170 (30). Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 70.98; H, 5.38; N, 4.10.

2-Acetoxy-4-methoxy-7-methyl-2,3,4,9-tetrahydro-[1]-benzopyrano[8,7-*b*][1,4]oxazin-9-one (7). A solution of monooxime **1** (328 mg, 1.5 mmol) in vinyl acetate (**6**) (4 mL) was refluxed for 4 d. The excess **6** was evaporated and the residue was chromatographed (silica gel, 1:1 *n*-hexane/ethyl acetate) to give **7** (148 mg, 32%): mp 142−144 °C (from ether); IR 1760, 1720, 1605 cm^{-1}; ^1H NMR δ 2.15 (s, 3H), 2.40 (s, 3H), 3.52 (dd, 1H, J = 2.5 and 11.4 Hz), 3.67 (dd, 1H, J = 3.1 and 11.4 Hz), 3.85 (s, 3H), 6.17 (s, 1H), 6.71 (dd, 1H, J = 2.5 and 3.1 Hz), 7.11 (d, 1H, J = 8.7 Hz), 7.19 (d, 1H, J = 8.7 Hz); ^{13}C NMR δ 18.8, 21.0, 50.6, 61.7, 89.7, 110.9, 111.5, 113.0, 115.6, 117.1, 129.1, 138.2, 152.4, 160.2, 169.0; mass spectrum *m*/*z* (rel intensity) 305 (M^+, 77), 275 (11), 273 (4), 263 (22), 234 (70), 233 (26), 232 (100), 214 (46), 203 (73). Anal. Calcd for $C_{15}H_{15}NO_6$: C, 59.01; H, 4.95; N, 4.59. Found: C, 58.88; H, 4.81; N, 4.39. Compound **1** (124 mg, 38%) was then eluted.

2-Butoxy-4-methoxy-7-methyl-2,3,4,9-tetrahydro-[1]benzopyrano[8,7-*b*][1,4]oxazin-9-one (9). A solution of **1** (219 mg, 1 mmol) in butyl vinyl ether (**8**) (3 mL) was refluxed for 60 h and then was chromatographed (silica gel, 2:1 up to 1:2 *n*-hexane/ethyl acetate) to give **9** (58 mg, 18%): oil; IR 1710, 1595 cm^{-1}; ^1H NMR δ 0.89 (t, 3H, J = 7.3), 1.30−1.39 (m, 2H), 1.56−1.67 (m, 2H), 2.38 (d, 3H, J = 1.0 Hz, 7-CH_3), 3.48 (dd, 1H, J = 2.6 and 11 Hz), 3.57 (dd, 1H, J = 3.4 and 11 Hz), 3.69 (dt, 1H, J = 6.8 and 9.9 Hz), 3.85 (s, 3H), 4.0 (dt, 1H, J = 6.8 and 9.9 Hz), 5.45 (dd, 1H, J = 2.6 and 3.4 Hz), 6.15 (q, 1H, J = 1.0 Hz), 7.08 (d, 1H, J = 8.6 Hz), 7.14 (d, 1H, J = 8.6 Hz); ^{13}C NMR δ 13.8, 18.8, 19.1, 31.4, 52.0, 61.5, 69.3, 96.9, 111.9, 112.6, 115.5, 116.3, 129.5, 138.5, 142.7, 152.7, 160.7; mass spectrum *m*/*z* (rel intensity) 319 (M^+, 39), 289 (19), 232 (100), 214 (14), 202 (84). Anal. Calcd for $C_{17}H_{21}NO_5$: C, 63.93; H, 6.62; N, 4.38. Found: C, 63.69; H, 6.81; N, 4.10.

Reaction of 1 with 3,4-Dihydro-2*H*-pyran (10). Preparation of Compounds 7-methoxy-4-methyl-7,7a,8,9,10,-11a-hexahydro-pyrano[2,3-*b*][1]benzopyrano[7,8-*e*][1,4]-oxazine (11) and 7-Methoxy-4-methyl-7,7a,9,10,11,11a-hexahydro-pyrano[3,2- *b*][1]benzopyrano[7,8-*e*][1,4]oxazine (12). A solution of compound **1** (328 mg, 1.5 mmol) in **10** (4 mL) was refluxed for 24 h. The excess **10** was evaporated, and the residue was chromatographed (silica gel, 1:2 *n*-hexane/ethyl acetate) to give as first fraction compound **11** (250 mg, 55%): mp 159−161 °C (from ether); IR 1720, 1610, 1290 cm^{-1}; ^1H NMR δ 1.5−1.9 (m, 3H), 1.95−2.04 (m, 1H), 2.38 (s, 3H), 3.71 (ddd, 1H, J = 2.5, 4.2, 10.3 Hz), 3.76 (dt, 1H, J = 3.5, 11.8 Hz), 3.82 (s, 3H), 4.07 (ddd, 1H, J = 4.5, 8.9, 11.8 Hz), 5.61 (d, 1H, J = 2.5 Hz), 6.15 (s, 1H), 7.01 (d, 1H, J = 8.7 Hz), 7.13 (d, 1H, J = 8.7 Hz); ^{13}C NMR δ 18.8, 20.3, 22.8, 54.8, 62.0, 62.1, 94.8, 111.6, 112.7, 115.5, 116.4, 129.5, 135.9, 142.1, 152.6, 160.6; mass spectrum *m*/*z* (rel intensity) 303 (M^+, 27), 281 (27), 273 (38), 272 (23), 242 (19), 216 (36), 207 (100). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.21; H, 5.68; N, 4.60. Compound **12** was then eluted (26 mg, 6%): mp 156−158 °C (from ether); IR 1720, 1610, 1270 cm^{-1}; ^1H NMR δ 1.5−2.13 (m, 4H), 2.37 (s, 3H), 3.63−4.1 (m, 2H), 3.86 (s, 3H), 4.56 (t, 1H, J = 3.0 Hz), 4.86 (s, 1H), 6.14 (s, 1H), 7.04 (d, 1H, J = 8.5 Hz), 7.11 (d, 1H, J = 8.5 Hz); ^{13}C NMR δ 19.4, 20.2, 28.9, 62.9, 67.4, 72.2, 81.9, 110.6, 112.9, 115.9, 116.7, 127.8, 135.9, 142.3, 151.8, 160.6; mass spectrum *m*/*z* (rel intensity) 303 (M^+, 20), 273 (22), 260 (13), 202 (22), 188 (18), 149 (100). Anal. Calcd for $C_{16}H_{17}NO_5$: C, 63.36; H, 5.65; N, 4.62. Found: C, 63.46; H, 5.68; N, 4.41.

Reaction of 1 with *N*-Methylmaleimide (13a). Preparation of Compounds 7-(Methoxyimino)-4-methyl-2,8-dioxo-2,6,7,8-tetrahydro-6,8a-ethano-[1]benzopyran-9,10-dicarboxylic Acid *N*-Methylimide (14a) and 2-(Methoxyimino)-5-methyl-1-oxo-1,2,7,8-tetrahydro-6,8α-ethanonaphthalene-7,8,9,10-tetracarboxylic Acid Bis(*N*-methylimide) (17a). A solution of **1** (300 mg, 1.37 mmol) and **13a** (304 mg, 2.7 mmol) in chlorobenzene (3 mL) was refluxed for 1 h. Compound **14a** was precipitated upon cooling as pale yellow crystals (279 mg, 61%): mp 288−291 °C dec (from methanol); IR 1770, 1718, 1690 cm^{-1}; ^1H NMR δ 1.98 (s, 3H), 2.95 (s, 3H), 3.34 (dd, 1H, J = 3.0 and 8.7 Hz), 3.55 (d, 1H, J = 8.7 Hz), 4.16 (s, 3H, CH_3O), 5.03 (dd, 1H, J = 3.0 and 6.6 Hz), 5.97 (s, 1H), 6.43 (d, 1H, J = 6.6 Hz); ^{13}C NMR (DMSO-d_6) δ 16.4, 25.0, 33.3, 40.2, 44.3, 63.8, 85.5, 116.8, 126.9, 132.0, 144.1, 146.7, 159.6, 173.3, 174.7, 184.9; mass spectrum *m*/*z* (rel intensity) 330 (M^+, 59), 299 (97), 271 (99), 186 (100), 158 (89), 130 (77), 115 (34), 103 (79). Anal. Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.30; H, 4.33; N, 8.60. The filtrate was chromatographed (silica gel, 2:3 *n*-hexane/ethyl acetate) to give compound **17a** (87 mg, 21%): mp 214−216 °C dec (from methanol); IR 1764, 1715, 1685 cm^{-1}; ^1H NMR δ 1.84 (s, 3H), 2.84 (s, 6H), 3.21 (dd, 2H, J = 2.9 and 8.4 Hz), 3.72 (t, 1H, J = 2.9 Hz), 3.74 (d, 2H, J = 8.4 Hz), 4.24 (s, 3H, CH_3O), 6.61 (d, 1H, J = 10.5 Hz), 6.92 (d, 1H, J = 10.5 Hz); ^{13}C NMR δ 17.9, 24.9, 41.0, 43.5, 48.3, 50.1, 64.2, 117.2, 125.2, 129.8, 137.9, 145.9, 174.8, 175.7, 191.9; mass spectrum *m*/*z* (rel intensity) 397 (M^+, 100), 366 (55), 338 (28), 311 (8), 281 (17), 170 (85), 143 (80), 112 (82), 83 (94). Anal. Calcd for $C_{20}H_{19}N_3O_6$: C, 60.45; H, 4.82; N, 10.57. Found: C, 60.31; H, 5.0; N, 10.31.

Reaction of 1 with *N*-Phenylmaleimide (13b). Preparation of Compounds 7-(Methoxyimino)-4-methyl-2,8-dioxo-2,6,7,8-tetrahydro-6,8a-ethano-[1]benzopyran-9,10-dicarboxylic Acid *N*-Phenylimide (14b) and 2-(Methoxyimino)-5-methyl-1-oxo-1,2,7,8-tetrahydro-6,8a-ethanonaphthalene-7,8,9,10-tetracarboxylic Acid Bis(*N*-phenylimide) (17b). A solution of **1** (219 mg, 1 mmol) and **13b** (260 mg, 1.5 mmol) in chlorobenzene (3 mL) was refluxed for 1 h. Compound **14b** was precipitated upon cooling of the reaction mixture, as pale yellow crystals (200 mg, 51%): mp 298−300 °C dec (from methanol); IR 1775, 1718, 1695 cm^{-1}; ^1H NMR (DMSO-d_6) δ 2.02 (s, 3H), 3.67 (dd, 1H, J = 2.5 and 8.3 Hz), 3.94 (d, 1H, J = 8.3 Hz), 4.09 (s, 3H), 4.83 (dd, 1H, J = 2.5 and 6.3 Hz), 6.03 (s, 1H), 6.97 (d, 1H, J = 6.3 Hz), 7.08 (d, 2H, J = 7.1 Hz), 7.38−7.54 (m, 3H); ^{13}C NMR (DMSO-d_6) δ 16.3, 33.6, 40.5, 44.4, 63.8, 85.5, 116.9, 126.8, 127.1, 128.9, 129.1, 131.6, 132.0, 144.0, 146.6, 159.5, 172.5, 173.9, 184.7; mass spectrum *m*/*z* (rel intensity) 392 (M^+, 53), 361 (82), 333 (94), 187 (90), 186 (100), 173 (72), 160 (90), 131 (80), 130 (74), 103 (75), 77 (82). Anal. Calcd for $C_{21}H_{16}N_2O_6$: C, 64.28; H, 4.11; N, 7.14. Found: C, 64.31; H, 4.17; N, 6.98.

The filtrate was chromatographed (silica gel, 1:0 up to 1:2 *n*-hexane/ethyl acetate) to give the imide **17b** (66 mg, 13%): mp 218−220 °C (from methanol); IR 1768, 1715, 1700, 1690 cm^{-1}; ^1H NMR δ 2.0 (s, 3H), 3.80 (t, 1H, J = 2.8 Hz), 4.09 (dd, 2H, J = 2.8 and 8.6 Hz), 4.25 (d, 2H, J = 8.6 Hz), 4.28 (s, 3H), 6.76 (d, 4H, J = 6.9 Hz), 6.83 (d, 1H, J = 10.6 Hz), 6.98 (d, 1H, J = 10.6 Hz), 7.25−7.34 (m, 6H); ^{13}C NMR δ 18.1, 41.5, 43.2, 49.1, 51.1, 64.3, 117.2, 125.7, 126.2, 128.6, 129.2, 129.4, 131.2, 139.9, 146.3, 175.0, 175.8, 193.2; mass spectrum *m*/*z* (rel intensity) 521 (M^+, 38), 491 (8), 463 (8), 318 (35), 201 (11), 173 (100), 170 (42), 91 (47), 77 (54). Anal. Calcd for $C_{30}H_{23}N_3O_6$ C, 69.09; H, 4.45; N, 8.06. Found: C, 68.83; H, 4.41; N, 7.81.

Reaction of 1 with Ethyl Acrylate (18). Preparation of Ethyl 7-(Methoxyimino)-4-methyl-2,8-dioxo-2,6,7,8-tetrahydro-6,8a-ethano-[1]benzopyran-9-carboxylate (19). A solution of compound **1** (328 mg, 1.5 mmol) in **18** (4 mL) was refluxed for 6 h and then chromatographed (silica gel, 2:3 *n*-hexane/ethyl acetate) to give **19** (200 mg, 42%): mp 138−140 °C (from ether); IR 1740, 1720, 1690, 1600 cm^{-1}; ^1H NMR δ 1.21 (t, 3H, J = 7.0 Hz), 1.87 (ddd, 1H, J = 2.8, 6.0 and 13.2 Hz), 2.08 (s, 3H), 2.35 (ddd, 1H, J = 2.8, 10.6 and 13.2 Hz), 3.31 (dd, 1H, J = 6.0 and 10.6 Hz), 4.10 (s, 3H), 4.11 (m, 2H, CH_2CH_3), 4.53 (dt, 1H, J = 2.8 and 6.8 Hz), 5.90 (s, 1H), 6.62 (d, 1H, J = 6.8 Hz); ^{13}C NMR δ 14.0, 17.1, 26.9, 31.8, 43.3, 61.8, 63.9, 86.3, 116.8, 127.4, 132.5, 146.1, 146.4, 159.1, 160.5, 170.8; mass spectrum *m*/*z* (rel intensity) 319 (M^+, 27), 288 (10), 274 (13), 260 (73), 232 (25), 214 (12), 186 (100), 158 (40). Anal. Calcd for $C_{16}H_{17}NO_6$: C, 60.18; H, 5.37; N, 4.39. Found: C, 60.13; H, 5.31; N, 4.41.

Supporting Information Available: ORTEP diagrams and X-ray crystallographic data[11] of compounds **7** and **17a** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(11) The authors have deposited full details of the X-ray structure determination of compounds **7** and **17a** with the Cambridge Crystallographic Data Centre. These data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.