Dioxopyrrolines. XLV.[1] [2+2] Photocycloaddition of 4-Ethoxycarbonyl-5-aryl-1*H*-pyrrole-2,3-dione to Cyclopentene Derivatives: Formation of Dihydropyridones

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Photocycloaddition reactions of 4-ethoxycarbonyl-5-aryl-1*H*-pyrrole-2,3-dione (1) with cyclopentadiene, indene, and cyclopentene gave the dihydropyridones 8, 11, and 12 as major products, respectively. Formation of them can be rationalized by assuming the formation of a 2s+2a adduct predicted by the stereoselection rule and subsequent skeletal rearrangement. The stereochemical results seem to support the hypothesis that the donor–acceptor interaction as theoretically deduced by Epiotis plays an important role in determining the stereochemical pathway of photocycloaddition.

Keywords photocycloaddition; dioxopyrroline; cyclopentadiene; cyclopentene; indene; dihydropyridone; hydroindole; cyclobutane; stereoselection rule; donor–acceptor interaction

Photocycloaddition of the dioxopyrroline **1** to acyclic olefins proceeds in a regio- and stereo-selective manner to give a head-to-tail (HT) cycloadduct, *exo*- or *endo*-substituted cyclobutanes **2**, accompanied in some cases with a dihydropyridone **3**.[2] The stereochemical results can be predicted by the stereo-selection rule proposed by us in the previous paper,[3] which states that weakly electron-donating olefins give a 2s+2a product (R in the structure **2**: *exo*), while strongly electron-donating olefins give a 2s+2s product (R in the structure **2**: *endo*) as the major products, both being formed from the favored *endo*-π-complex. Dihydrofurans give dihydropyridones **4** and 2,4-dioxa-10-azatricyclo[6.3.0.^{1,8}0^{3,7}]undecanes **5**,[4] which are also considered to be the products predicted by the stereoselection rule to be formed from **6** and **7**, respectively. When cycloalkenes, particularly cyclopentene derivatives, were used as a cycloaddend, the major product was a dihydropyridone.[5] This paper deals with this subject in detail.

Results and Discussion

Irradiation of a solution of the dioxopyrroline **1a** and cyclopentadiene in dimethoxyethane (DME) for 1 h with $\geqq$300 nm light afforded three adducts **8a**, **9a**, and **10a** in yields of 24%, 17%, and 10%, respectively. Benzocyclopentene (indene) on similar irradiation gave **11a** as a sole adduct in 40% yield. Cyclopentene afforded **12a** as a sole characterizable adduct, although the yield was less satisfactory (10%). The *N*-methyldioxopyrroline **1b** on similar photoaddition to cyclopentadiene afforded **8b** as an only isolable product (11%). Indene gave **11b** in 18% yield, but cyclopentene gave no charaterizable products. Heating of a solution of the dioxopyrroline **1a** or **1b** and cyclopentadiene in dioxane at 160 °C did not give any adduct.[6]

The dihydropyridone structures of the major products **8a**, **b**, **11a**, **b** and **12a** were elucidated as follows. All of them

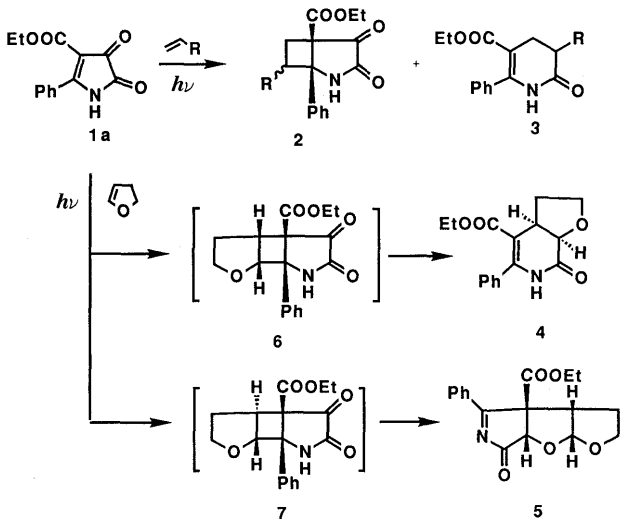

Chart 1

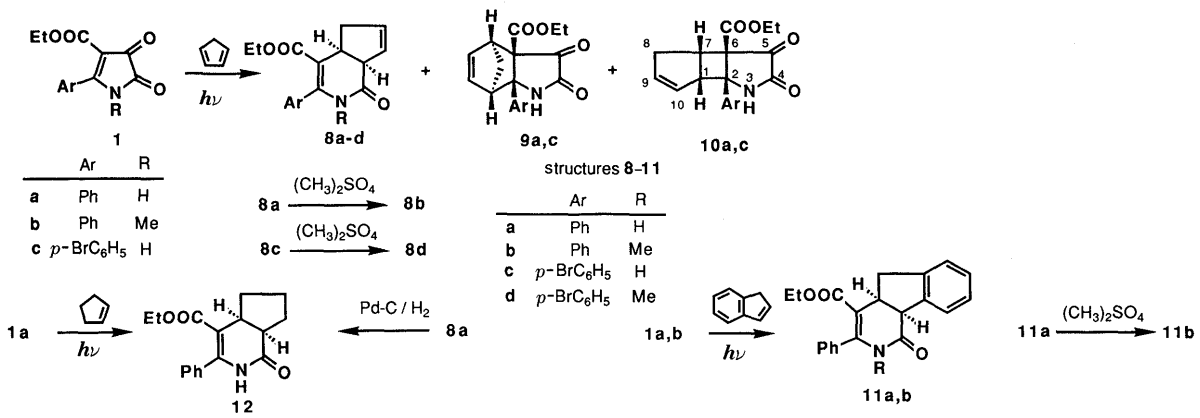

Chart 2

have the molecular formulae corresponding to the 1 : 1 adduct minus CO, and they have similar spectral characteristics. The proton and carbon-13 nuclear magnetic resonance (^{1}H- and ^{13}C-NMR) spectra (see Experimental) supported the above assignments and suggested their structures. In the infrared (IR) spectra they lack the absorption due to the five-membered ring keto-group, but exhibit bands due to a six-membered ring lactam carbonyl group at around 1630 cm^{-1}. In the ultraviolet (UV) spectra they have a strong absorption around 285 nm which is attributable to the dihydropyridone moiety.[2)]

Each adduct was chemically correlated. Hydrogenation of **8a** over 5% Pd–C afforded **12a**. Methylation of **8a** and **11a** with dimethyl sulfate afforded the *N*-methyl derivatives, which were identical with **8b** and **11b**, respectively.

The other adducts **9a** and **10a** have the same molecular formula $C_{18}H_{17}NO_4$ corresponding to the 1 : 1 adduct of the addends. Their ^{1}H- and ^{13}C-NMR spectra as well as the IR spectra suggested that they are a hydroindole and a cyclobutane, respectively, except for the stereochemistries. The *cis* relationship of the hydrogens on the ring juncture was indicated for **10a** by an ^{1}H-NMR triple resonance experiment, which revealed that the coupling constant between the protons (C_1 and C_7) was 7 Hz on simultaneous irradiation of the protons at δ 2.58 (H_8) and 5.93 (H_{10}). Howevere, two possible stereo-structures, *cis-syn-cis* and *cis-anti-cis* still remained.

Final clarifications of the structures including the stereochemistry of all products were obtained by X-ray analyses. The samples for this purpose were prepared as follows. Irradiation of the 5-*p*-bromophenyldioxopyrroline **1c** in the presence of cyclopentadiene also gave three adducts **8c**, **9c** and **10c** in yields of 22%, 28% and 5%, respectively. Methylation of **8c** with dimethyl sulfate afforded the corresponding *N*-methyl derivative **8d**. The spectral resemblance confirmed that they correspond to **8a**, **9a**, and **10a**, respectively. Among them **8d** and **9c** were subjected to X-ray analyses,[5a)] which unequivocally established that **8d** is the dihydropyridone and **9c** is the hydroindole with the stereochemistries shown in Chart 2. Although the bromo compound **10c** did not give crystals suitable for X-ray analysis, **10a** crystallized from Et_2O–CH_2Cl_2–methanol as prisms was successfully analysed by X-ray crystallography,[7)] that established **10a** to be a cyclobutane of *cis-syn-cis* stereochemistry.

Here we discuss how these compounds were formed (Charts 3 and 4). In this photocycloaddition, two transition states due to the difference of approach of two the addends are possible, *i.e.*, an *endo-* and an *exo-*π-complex.[8)] The former transition state should be favored over the latter, since the two addends are sufficiently planar and gain a maximum overlap of orbitals in the former complex. It is reasonable to assume that the dioxopyrroline–cyclopentadiene is a polar pair, as is the dioxopyrroline–butadiene pair,[3)] and in such a case the stereo-selection rule predicts that in the favored *endo-*π-transition an s+a process is favored over an s+s process (or the first bond formation at C(α) of the carbonyl group occurs with retention and the second bond formation at C(β) of the carbonyl occurs with inversion of the stereochemistry), and since the dioxopyrroline ring is stereochemically rigid, the antarafacial component is the diene, giving rise to the cyclobutane of *cis-syn-trans* configuration **17** as the major adduct, accompanied with a minor s+s adduct, the cyclobutane of *cis-syn-cis* configuration **10a**. Since the major cyclobutane **17** has highly strained *trans*-fused ring juncture, it would immediately undergo further skeletal change. The concerted [1,3] shift of the C_1–C_2 bond to C_4 through a lactim form gives the azanorbornene **18** which would collapse to the dihydropyridone **8a** by a cheletropic loss of CO.[9)] In fact, a similar reaction was visualized as the thermal reaction of the imidate **13** of the cyclobutane to form the dihydropyridine **14**.[10)] Similarly, the imidate **15** prepared from the cyclobutane **10a** by alkylation with triethyloxonium fluoroborate, on heating in toluene at 200 °C for 6 h gave **8a** in 60% yield after hydrolysis of the pyrolysate.

The other [1,3] shift, migration of the C_1–C_2 bond to C_9, gives the hydroindole **9a**. A similar reaction was also observed in thermolysis of the *exo*-vinyl cyclobutane **2** (R: CH_2=CH–) to form the hydroindole **16**.[11)] The above hydroindole **9a** must not be the direct 1,4-cycloaddition product, since the [4s+2s] addition from the *endo-*π-complex would give the stereoisomer **20**. In the above transformation, **10a** must not be the intermediate of **8a** or **9a**, since **10a** itself gave neither **8a** nor **9a** on irradiation (1 h) or on thermolysis (200 °C, 6 h).[12)]

The stereo-selection rule also predicts that in the less favored transition *via* the *exo-*π-complex, a 2s+2s addition is favored to give the cyclobutane of *cis-anti-cis* configuration **19**. However, this cyclobutane should not be an intermediate for either **8a** or **9a** since a concerted [1,3] shift for **8a** is impossible for steric reasons and the other [1,3] shift for hydroindole would produce the stereoisomer **20**.

This result seems to support our consideration that in the dioxopyrroline–olefin photocyclization the donor–acceptor interaction plays an important role in determining the stereochemical pathway of the reaction. Our argument on this cycloaddition is essentially in accordance with Epiotis's donor–acceptor interaction in enone–olefin photocycloaddition.[13)] However, we should mention that in this cycloaddition the olefin (donor) plays a role as an antarafacial component, in contrast to the suggestion by Epiotis that the enone (acceptor) acts as the antarafacial one. This must be due to stereochemical rigidity of the five

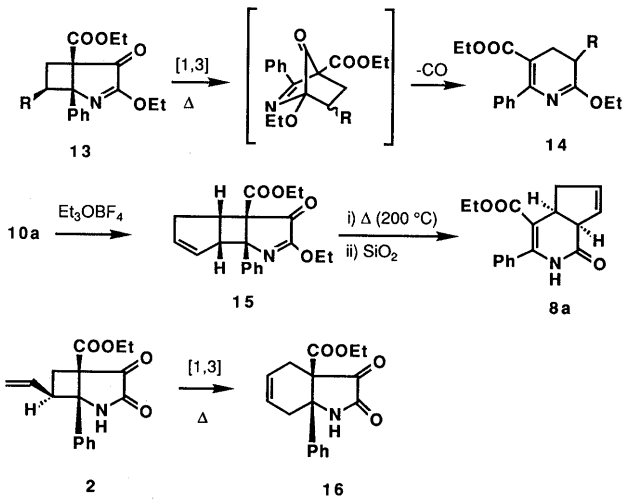

Chart 3

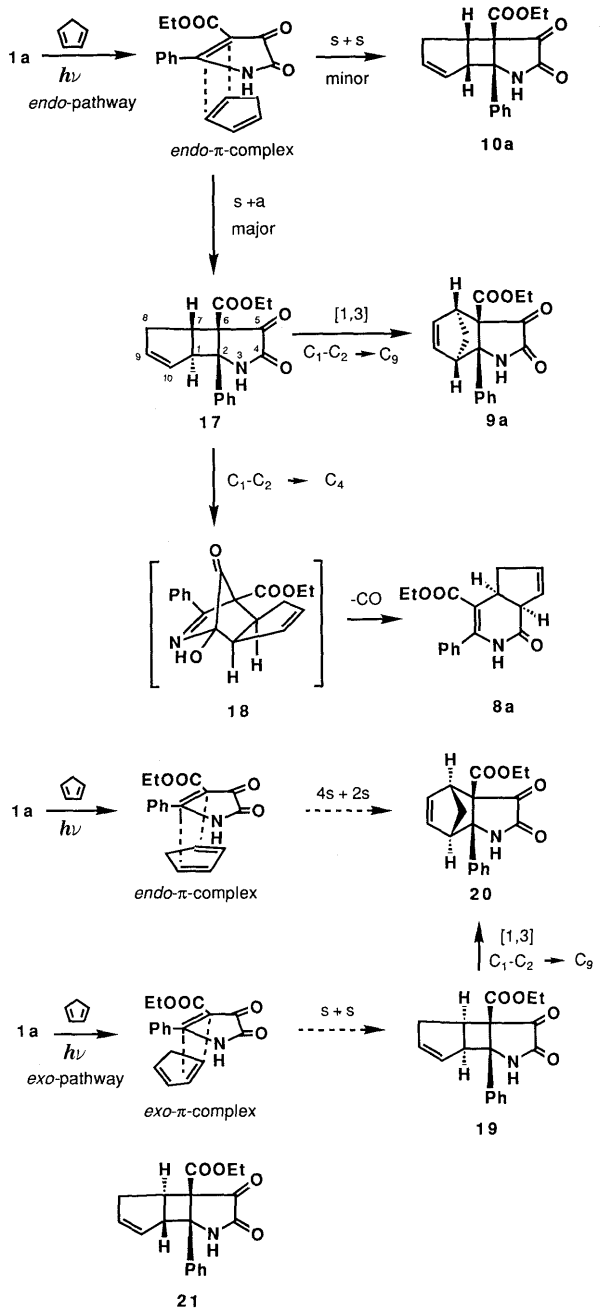

Chart 4

membered dioxopyrroline (acceptor) and suggests that various electron transition configurations may be operating in such a complicated system.

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were taken on a Yanagimoto micro hot-stage melting point apparatus, and are uncorrected. IR spectra were taken in Nujol mulls with a Hitachi 260-10 spectrophotometer and are given in cm^{-1}. UV spectra were measured in ethanol with a Hitachi 200-10 spectrophotometer and are given in λ_{max} nm (ε). ^{1}H-NMR (100 MHz) and ^{13}C-NMR (25.0 MHz) spectra were taken in $CDCl_3$ solution with tetramethylsilane (TMS) as an internal standard on a JEOL FX-100 spectrometer. Thin layer chromatography (TLC) was performed on precoated Silica gel 60 F_{254} plates (Merck). The photolysis solution was irradiated internally using a 300 W high-pressure mercury lamp (Eikosha Halos PIH 300) with a Pyrex filter. The synthesis of the dioxopyrrolines **1a**—**c** was reported previously.[14]

Photocycloaddition of 1a with Cyclopentadiene The reaction was carried out according to the procedure reported in the previous paper.[7] The products, yields, physical and spectral data are as follows.

4-Ethoxycarbonyl-3-phenyl-4a,7a-dihydrocyclopenta[3,4-*c*]pyridin-6-en-1(2*H*)-one (**8a**): Yield 24%, mp 108—110 °C, colorless needles from CH_2Cl_2–Et_2O. IR: 3250, 3100, 1670, 1640, 1600. UV: 285 (9000). ^{1}H-NMR: 0.91 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.28—2.51 (1H, m, C_{7a}-H), 2.91—3.18 (1H, m, C_{4a}-H), 3.58—3.70 (2H, m, C_5-H), 3.92 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.94 (2H, s, C_6 and C_7-H), 7.45—7.70 (5H, m, Ar-H). ^{13}C-NMR: 13.2 (q, $COOCH_2\underline{C}H_3$), 37.3 (d, C_{4a}), 41.5 (t, C_5), 48.0 (d, C_{7a}), 59.5 (d, $COO\underline{C}H_2CH_3$), 107.9 (s, C_4), 127.2 (d, 2C, Ph), 127.8 (d, 2C, Ph), 128.0 (d, C_6), 128.6 (d, Ph), 131.7 (d, C_7), 135.7 (s, Ph), 142.9 (s, C_3), 166.6 (s, C_1), 169.7 (s, $\underline{C}OOCH_2CH_3$). *Anal.* Calcd for $C_{17}H_{17}NO_3$: C, 72.06; H, 6.05; N, 4.94. Found: C, 71.88; H, 5.98; N, 4.87.

(3a*S**,4*S**,7*S**,7a*S**)-3a-Ethoxycarbonyl-7a-phenyl-2,3,3a,4,7,7a-hexahydro-4,7(methano)-indole-2,3-dione (**9a**): Yield 17%, mp 167—168 °C, colorless prisms from CH_2Cl_2–Et_2O. IR: 3170, 3100, 1780, 1740, 1720. UV: 352 (4000). ^{1}H-NMR: 0.76 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.75 (2H, AB_q, J=14, 10 Hz, C_8-H), 3.17 (1H, br s, C_7-H), 3.35 (1H, br s, C_4-H), 3.60—3.90 (2H, m, $COOC\underline{H}_2CH_3$), 6.30 (1H, dd, J=3, 5 Hz, C_5-H), 6.80 (1H, dd, J=3, 5 Hz, C_6-H), 7.2—7.5 (5H, m, Ar-H). *Anal.* Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.23; H, 5.41; N, 4.48.

6-Ethoxycarbonyl-2-phenyl-3-azatricyclo[5.3.0.^{1,7}0^{2,6}]dec-9-ene-4,5-dione (**10a**): Yield 10%, mp 202—203 °C, colorless prisms from CH_2Cl_2–Et_2O. IR: 3170, 1760, 1740, 1720. ^{1}H-NMR: 0.68 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.58 (2H, br s, C_8-H), 3.64 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 3.86 (1H, six, J=7 Hz, C_7-H), 4.08—4.18 (1H, m, C_1-H), 5.63 (1H, br d, J=6 Hz, C_9-H), 5.93 (1H, br d, J=6 Hz, C_{10}-H), 7.3—7.6 (5H, m, Ar-H). *Anal.* Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.50. Found: C, 69.18; H, 5.39; N, 4.22.

Photocycloaddition of 1a with Indene A solution of **1a** (2.5 g) and indene (11 g) in DME (300 ml) was irradiated at 0 °C for 1 h. After removal of the solvent, the residue in benzene was chromatographed over SiO_2. Elution with benzene and crystallization of the eluate from Et_2O gave 4-ethoxycarbonyl-3-phenyl-4a,9b-dihydroindeno[1,2-*c*]pyridin-1(2*H*,5*H*)-one (**11a**) (1.40 g, 40%), colorless prisms, mp 194—195 °C. IR: 3200, 3100, 1700, 1670, 1650, 1610. UV: 287 (9400). ^{1}H-NMR: 0.93 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.8—3.1 (1H, m, C_{9b}-H), 3.3—3.5 (1H, m, C_{4a}-H), 3.7—4.07 (2H, m, C_5-H), 3.93 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 7.2—7.6 (9H, m, Ar-H). *Anal.* Calcd for $C_{21}H_{19}NO_3$: C, 75.65; H, 5.74; N, 4.20. Found: C, 75.65; H, 5.62; N, 4.14.

Photocycloaddition of 1a with Cyclopentene A solution of **1a** (2.5 g) and cyclopentene (5.5 g) in DME (350 ml) was irradiated at 0 °C for 1 h. After removal of the solvent, the residue in benzene was chromatographed over SiO_2. Elution with benzene and crystallization of the product from Et_2O–hexane gave 4-ethoxycarbonyl-3-phenyl-4a,7a-dihydrocyclopenta[3,4-*c*]pyridin-1(2*H*)-one (**12**) (320 mg, 10%), colorless prisms, mp 143—144 °C. IR: 3200, 3100, 1700sh, 1670, 1640. UV: 286 (11000). ^{1}H-NMR: 0.92 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.5—2.4 (8H, m, C_{4a}, C_5, C_6, C_7 and C_{7a}-H), 2.7—3.2 (2H, m, $COOC\underline{H}_2CH_3$), 7.4 (5H, m, Ar-H). *Anal.* Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91. Found: C, 71.40; H, 6.62; N, 4.66.

Photocycloaddition of 1b with Cyclopentadiene A solution of **1b** (3.0 g) and cyclopentadiene (8.5 g) in DME (300 ml) was irradiated at −30 °C for 45 min. After removal of the solvent, the residue in benzene was chromatographed over Al_2O_3. Elution with benzene gave a brown gummy material which in hexane was again chromatographed over Al_2O_3. Elution with hexane–benzene (1 : 1) and crystallization of the product from hexane gave 4-ethoxycarbonyl-2-methyl-3-phenyl-4a,7a-dihydrocyclopenta[3,4-*c*]pyridin-6-en-1(2*H*)-one (**8b**) (378 mg, 11%) as colorless prisms, mp 89—91 °C. IR: 1670, 1630, 1600. UV: 286 (10000). ^{1}H-NMR: 0.87 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.77 (3H, s, NCH_3), 2.2 (1H, m, C_{7a}-H), 3.2 (1H, m, C_{4a}-H), 3.67 (2H, m, C_5-H), 3.87 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 6.03 (2H, br s, C_6 and C_7-H), 7.1—7.6 (5H, m, Ph). ^{13}C-NMR: 13.7 (q, $COOCH_2\underline{C}H_3$), 32.3 (q, NCH_3), 36.9 (d, C_{4a}), 41.7 (t, C_5), 48.7 (d, C_{7a}), 59.9 (t, $COO\underline{C}H_2CH_3$), 112.5 (s, C_4), 129.4 (d, 3C, Ph and C_6), 130.1 (d, 2C, Ph), 130.5 (d, Ph), 133.1 (d, C_7), 137.1 (s, Ph), 148.4 (s, C_3), 168.9 (s, C_1), 172.3 (s, $\underline{C}OOCH_2CH_3$). HRMS *m/z*: M^+ Calcd for $C_{18}H_{19}NO_3$: 297.1366. Found: 297.1386.

Photocycloaddition of 1b with Indene A solution of **1b** (1.565 g) and indene (5.5 g) in DME (300 ml) was irradiated at 0 °C for 2 h. After removal of the solvent *in vacuo* the residue in benzene was chromatographed over SiO_2. Elution with benzene–hexane (1 : 1) gave 4-ethoxycarbonyl-2-methyl-3-phenyl-4a,9b-dihydroindeno[1,2-*c*]pyridin-1(2*H*,5*H*)-one (**11b**) (370 mg, 18%) as colorless prisms from CH_2Cl_2–Et_2O–hexane, mp 117—118 °C. IR: 1680, 1630. UV: 286 (7200). ^{1}H-NMR: 0.89 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.76 (3H, s, NCH_3), 2.95 (1H, dd, J=9,

15 Hz, C_5-H), 3.50 (1H, dd, J=7, 15 Hz), 3.7 (1H, m, C_{4a}-H), 3.89 (2H, q, J=7 Hz, $COOCH_2CH_3$), 4.13 (1H, d, J=9 Hz, C_{9b}-H), 7.2—7.65 (9H, m, Ar-H). ^{13}C-NMR: 13.7 (q, $COOCH_2CH_3$), 32.5 (q, NCH_3), 39.0 (d, C_{4a}), 40.1 (t, C_5), 49.0 (d, C_{9b}), 60.0 (t, $COOCH_2CH_3$), 110.7 (s, C_4), 123.9 (d, Ar), 126.8 (d, Ar), 127.7 (d, Ar), 128.7 (d, 2C, Ar), 129.3 (d, 2C, Ar), 129.5 (d, 2C, Ar), 135.7 (s, Ar), 140.5 (s, C_{4a}), 141.4 (s, C_{9b}), 147.6 (s, C_3), 167.3 (s, C_1), 169.5 (s, $COOCH_2CH_3$). HRMS m/z: M^+ Calcd for $C_{22}H_{21}NO_3$: 347.1519. Found: 347.1514.

Methylation of 8a with Dimethyl Sulfate A solution of **8a** (100 mg) and dimethyl sulfate (1 ml) in CH_3CN (5 ml) was treated with 10% NaOH (0.5 ml) for 4 h at room temperature. The mixture was diluted with water and extracted with Et_2O. The extract was washed with 2% NaOH, 5% HCl and water, dried over Na_2SO_4, and evaporated. The residue was passed through a short column of Al_2O_3 to give **8b** (85 mg). This product was identical with the compound obtained from the photoaddition described above.

Methylation of 11a with Dimethyl Sulfate A solution of **11a** (80 mg) and dimethyl sulfate (1 ml) in CH_3CN (5 ml) was treated with 10% NaOH (1 ml) in the manner described above. The product was passed through a short column of SiO_2 to give **11b** (75 mg). This was identical with the compound obtained by the photoaddition described above.

Catalytic Hydrogenation of 8a A solution of **8a** (50 mg) in ethanol (50 ml) was hydrogenated over 5% Pd–C (100 mg) under atomospheric pressure at room temperature. After removal of the catalyst by filtration, the solvent was evaporated *in vacuo* to give **12** (48 mg, 95%). This was identical with the compound described above.

Photocycloaddition of 1c with Cyclopentadiene A solution of **1c** (2.0 g) and cyclopentadiene (6 g) in DME (200 ml) was irradiated at −30 °C for 1 h. After removal of the solvent, the residue was chromatographed over Al_2O_3. Elution with benzene and crystallization of the product from CH_2Cl_2–Et_2O gave 3-(*p*-bromophenyl)-4-ethoxycarbonyl-4a,7a-dihydrocyclopenta[3,4-*c*]pyridin-6-en-1(2*H*)-one (**8c**) (262 mg, 11%) as colorless needles, mp 168—170 °C. IR: 3250, 1700, 1690, 1635. UV: 285 (11000). ^{1}H-NMR: 0.98 (3H, t, J=7 Hz, $COOCH_2CH_3$), 2.4 (1H, m, C_{7a}-H), 3.0 (1H, m, C_{4a}-H), 3.7 (2H, m, C_5-H), 3.98 (2H, q, J=7 Hz, $COOCH_2CH_3$), 5.97 (2H, br s, C_6 and C_7-H), 7.17 (2H, d, J=9 Hz, ArH), 7.53 (2H, d, J=9 Hz, ArH). ^{13}C-NMR: 13.9 (q, $COOCH_2CH_3$), 37.6 (d, C_{4a}), 41.9 (t, C_5), 48.3 (d, C_{7a}), 60.2 (t, $COOCH_2CH_3$), 108.7 (s, C_4), 123.4 (s, Ar), 128.4 (d, C_6), 129.4 (d, 2C, Ar), 131.5 (d, 2C, Ar), 132.1 (d, C_7), 134.9 (s, Ar), 142.3 (s, C_3), 166.7 (s, C_1), 170.2 (s, $COOCH_2CH_3$). HRMS m/z: M^+ Calcd for $C_{17}H_{16}BrNO_3$: 361.0312 and 363.0288. Found: 361.0329 and 363.0232.

Further elution with benzene–CH_2Cl_2 (1 : 1) and crystallization of the product from Et_2O–EtOH gave 2-(*p*-bromophenyl)-6-ethoxycarbonyl-3-azatricyclo[5.3.0.^{1,7}0^{2,6}]dec-9-ene-4,5-dione (**10c**) (50 mg, 5%) as colorless needles, mp 216—218 °C. IR: 3170, 1760, 1735, 1700. UV: 230 (21700), 260 (7800). ^{1}H-NMR: 0.80 (3H, t, J=7 Hz, $COOCH_2CH_3$), 2.60 (2H, br s, C_8-H), 3.73 (2H, q, J=7 Hz, $COOCH_2CH_3$), 3.88 (1H, m, C_7-H), 4.10 (1H, m, C_1-H), 5.60 (1H, m, C_9-H), 5.95 (1H, m, C_{10}-H), 7.39 (2H, d, J=10 Hz, ArH), 7.58 (2H, d, J=10 Hz, ArH), 9.78 (1H, br s, NH). ^{13}C-NMR: 13.5 (q, $COOCH_2CH_3$), 34.0 (t, C_8), 37.3 (d, C_1), 56.4 (d, C_1), 61.6 (t, $COOCH_2CH_3$), 62.0 (s, C_6), 65.1 (s, C_7), 127.2 (d, 2C, Ar), 130.4 (d, C_9), 131.9 (d, 2C, Ar), 135.7 (s, Ar), 138.2 (d, C_{10}), 163.9 (s, C_4), 165.5 (s, $COOCH_2CH_3$), 192.3 (s, C_5). HRMS m/z: M^+ Calcd for $C_{18}H_{16}BrNO_4$: 389.0262 and 391.0332. Found: 389.0285 and 391.0340.

Further elution with CH_2Cl_2–benzene (1 : 1) and crystallization of the product from acetone-hexane gave (3a*S**,4*S**,7*S**,7a*S**)-7a-(*p*-bromophenyl)-3a-ethoxycarbonyl-2,3,3a,4,7,7a-hexahydro-4,7(methano)-indole-2,3-dione (**9c**) (400 mg, 22%) as colorless prisms, mp 200—202 °C. IR 3170, 1775, 1730, 1720. UV: 228 (22000). ^{1}H-NMR: 0.83 (3H, t, J=7 Hz, $COOCH_2CH_3$), 1.70 (2H, br s, C_8-H), 3.13 (1H, m, C_4-H), 3.38 (1H, m, C_7-H), 3.73 (2H, oct, $COOCH_2CH_3$), 6.25 (1H, m, C_5-H), 6.78 (1H, m, C_6-H), 7.17 (2H, d, J=9 Hz, ArH), 7.42 (2H, d, J=9 Hz, ArH). ^{13}C-NMR: 13.4 (q, $COOCH_2CH_3$), 45.5 (t, C_8), 50.6 (d, C_4), 54.2 (d, C_7), 62.0 (t, $COOCH_2CH_3$), 70.0 (s, C_{3a}), 71.9 (s, C_{7a}), 122.0 (s, Ar), 128.5 (d, 2C, Ar), 131.1 (d, 2C, Ar), 136.4 (d, C_5), 137.6 (s, Ar), 139.1 (d, C_6), 162.0 (s, C_2), 167.6 (s, $COOCH_2CH_3$), 195.7 (s, C_3). HRMS m/z: M^+ Calcd for $C_{18}H_{16}BrNO_4$: 389.0262 and 391.0332. Found: 389.0308 and 391.0344.

Methylation of 8c with Dimethyl Sulfate A solution of **8c** (80 mg) and dimethyl sulfate (1 ml) in CH_3CN (5 ml) was treated with 10% NaOH (1 ml) as described above. The product in benzene was passed through a short column of Al_2O_3 to give **8d** (75 mg), colorless prisms from *n*-hexane, mp 103—104 °C. IR: 1680, 1640. UV: 288 (9800). ^{1}H-NMR: 0.95 (3H, t, J=7 Hz, $COOCH_2CH_3$), 2.20—2.43 (1H, m, C_5-H), 2.74 (3H, s, NCH_3), 2.97—3.14 (1H, m, C_5-H), 3.40—3.70 (2H, m, C_{4a} and C_{7a}-H), 3.90 (2H, q, J=7 Hz, $COOCH_2CH_3$), 5.99 (2H, s, C_6 and C_7-H), 7.06 (2H, d, J=9 Hz, Ar-H), 7.56 (2H, d, J=9 Hz, Ar-H). ^{13}C-NMR: 13.7 (t, $COOCH_2CH_3$), 32.3 (q, NCH_3), 36.8 (d, C_{4a}), 41.7 (t, C_5), 48.6 (d, C_{7a}), 60.2 (t, $COOCH_2CH_3$), 111.3 (s, C_4), 122.8 (s, Ar), 129.6 (d, 2C, Ar), 130.5 (d, C_6), 131.6 (d, 2C, Ar), 132.0 (d, C_7), 134.8 (s, Ar), 145.9 (s, C_3), 145.9 (s, C_3), 167.1 (s, C_1), 170.2 (s, $COOCH_2CH_3$). HRMS m/z: M^+ Calcd for $C_{18}H_{18}BrNO_3$: 375.0469 and 377.0449. Found: 375.0496 and 377.0481.

Imidation of 10a with Triethyloxonium Fluoroborate A solution of **10a** (200 mg) in CH_2Cl_2 (10 ml) was treated with excess Et_3OBF_4 at room temperature for 5 h. The mixture was diluted with CH_2Cl_2, washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated. The residue was passed through a short column of SiO_2 and recrystallization of the eluate from Et_2O–hexane gave **15** (94 mg, 43%) as colorless prisms, mp 113—115 °C. IR: 1740, 1730, 1695, 1610. ^{1}H-NMR: 0.65 (3H, t, J=8 Hz, $COOCH_2CH_3$), 1.50 (3H, t, J=8 Hz, OCH_2CH_3), 2.55 (2H, m, CH_2), 3.60 (4H, m, OCH_2CH_3 overlapped with 2×CH), 4.50 (2H, m, $COOCH_2CH_3$), 5.50 and 5.90 (each 1H, m, olefinic H), 7.3—7.7 (5H, m, ArH). HRMS m/z: M^+ Calcd for $C_{20}H_{21}NO_4$: 339.1470. Found: 339.1495.

Pyrolysis of the Imidate 15 A solution of **15** (82 mg) in toluene (5 ml) was heatd in a sealed tube at 200 °C for 1 h. After evaporation of the solvent, the residue was treated with 5% HCl–EtOH at room temperature for 1 h. The mixture was diluted with water and extracted with CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$ and evaporated. The residue in benzene was chromatographed over SiO_2 gave **8a** (34 mg, 50%). This product was identical with the compound obtained from the photoaddition described above.

References and Notes

1) Part XLIV: T. Sano, Y. Horiguchi, K. Tanaka, and Y. Tsuda, *Chem. Pharm. Bull.*, **38**, 36 (1990).
2) T. Sano, Y. Horiguchi, Y. Tsuda, K. Furuhata, H. Takayanagi, and H. Ogura, *Chem. Pharm. Bull.*, **35**, 9 (1987).
3) T. Sano, Y. Horiguchi, and Y. Tsuda, *Chem. Pharm. Bull.*, **35**, 23 (1987).
4) T. Sano, M. Hirose, Y. Horiguchi, H. Takayanagi, H. Ogura, and Y. Tsuda, *Chem. Pharm. Bull.*, **35**, 4730 (1987).
5) Preliminary communications: *a*) Y. Tsuda, M. Kaneda, Y. Itatani, T. Sano, and H. Horiguchi, *Heterocycles*, **9**, 153 (1978); *b*) T. Sano, Y. Horiguchi, Y. Tsuda, and Y. Itatani, *ibid.*, **9**, 161 (1978).
6) We reported in the preliminary communication[5a] that a solution of **1a** and cyclopentadiene, when kept in a dark place for 2 weeks at room temperature gave the same adducts **8a**, **9a**, and **10a** in yields of 3, 2, and 1%, respectively. However, the yields of the products are too low for it to be plausible that they are the thermal products. The possibility that they are the photolytic products even under these conditions cannot be excluded.
7) T. Sano, Y. Horiguchi, H. Takayanagi, H. Ogura, and Y. Tsuda, *Chem. Pharm. Bull.*, **36**, 3130 (1988).
8) These two complexes are not essentially different from those of dihydrofuran,[4] since if we slide one component in one complex, the other complex is obtained. Therefore, we consider that in the dioxopyrroline–cyclopentadiene complex only one form (*endo*) will be produced for the reason discussed in the text.
9) In the preliminary communication[5a] we assumed that **8a** is formed from **21** by a stepwise biradical mechanism through C_6–C_7 bond rotation. However, evidence has become available that 1,3-shift of the C_1–C_2 bond to C_4 through the lactim form can occur.[1] If so, the concerted 1,3-shift in **21** is sterically impossible. Therefore **9a** and **8a** must be produced from the same intermediate **17**.
10) T. Sano, Y. Horiguchi, and Y. Tsuda, *Heterocycles*, **16**, 889 (1981).
11) T. Sano, Y. Horiguchi, S. Kambe, J. Toda, J. Taga, and Y. Tsuda, *Heterocycles*, **16**, 893 (1981).
11) We described in the preliminary communication[5a] that pyrolysis of **10a** yielded **9a** in a minute amount (TLC detection). However, in a repeated experiment we could not confirm this result.
13) N. D. Epiotis, *J. Am. Chem. Soc.*, **94**, 1941 (1972).
14) T. Sano, Y. Horiguchi, J. Toda, K. Imafuku, and Y. Tsuda, *Chem. Pharm. Bull.*, **32**, 497 (1984).