Dioxopyrrolines. LV.[1] Stereochemical Pathway of [2+2] Photocycloaddition Reaction of 4,5-Diethoxycarbonyl-1*H*-pyrrole-2,3-dione to Cycloalkadienes and Cycloalkenes

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The photocycloaddition reactions of 4,5-diethoxycarbonyl-1*H*-pyrrole-2,3-dione (6) to cycloalkadienes and cycloalkenes were examined. The addition of cyclopentadiene gave the hydroindole 8a (s+a product) as a major product and the *cis*-fused cyclobutane 7a (s+s product) as a minor one. In contrast, the addition of cyclohexadiene gave the cyclobutane 7b (s+s product) as a major product and the hydroindole 8b (s+a product) as a minor one. The photocycloaddition of cyclopentene, cyclohexene, and indene proceeded predominantly in an s+s manner to give the *cis-syn-cis* cyclobutanes, 16, 18, and 19, respectively. The stereochemical results were compared with those of the photocycloaddition reactions of 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione (1) to the corresponding cyclo-olefins, revealing that the steric relationship of the addends plays an important role in determining the stereochemical pathway of the reaction.

Keywords photocycloaddition; dioxopyrroline; cyclobutane; stereochemistry; stereo-selection rule; steric effect

The stereo-selection rule[2] for enone–olefin photocycloaddition seems to work reliably for rationalizing the stereochemical results observed in the photocycloaddition reactions of dioxopyrroline–olefin pairs.[3] The examples hitherto presented indicate that the polarity (the magnitude of donor–acceptor interaction) of the pair in the excited π-complex plays an important role in determining the stereochemical pathway of the reaction: an s+s product from a non-polar pair and an s+a product from a polar pair. The donor–acceptor interaction could be evaluated not only in terms of the electronic properties of the addends,[3a–c] but also, more importantly, in terms of their steric relationship.[3d,e] For example, photocycloaddition of 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione (**1**, 4-COOEt-5-Ph-dioxopyrroline) to cyclopentadiene gave the products **4a** and **5a**, derived from the s+a addition as the major products, and the s+s adduct **3a** as a minor product,[3c] while the dioxopyrroline–cyclohexadiene pair gave the s+s adduct **3b** as a major product, and the dihydropyridone **4b** and the hydroindole **5b** as minor products (Chart 1).[3d] This change of stereochemical pathway was considered to originate from the difference of polarity of the donor–acceptor pair, which is polar for the dioxopyrroline–cyclopentadiene pair and non-polar for the dioxopyrroline–cyclohexadiene pair. The decrease of polarity in the latter pair was attributed to the steric effect (puckering effect of the ethano-bridge in cyclohexadiene), which increases the donor–acceptor distance in the transition state and therefore decreases the magnitude of donor–acceptor interaction.[3d]

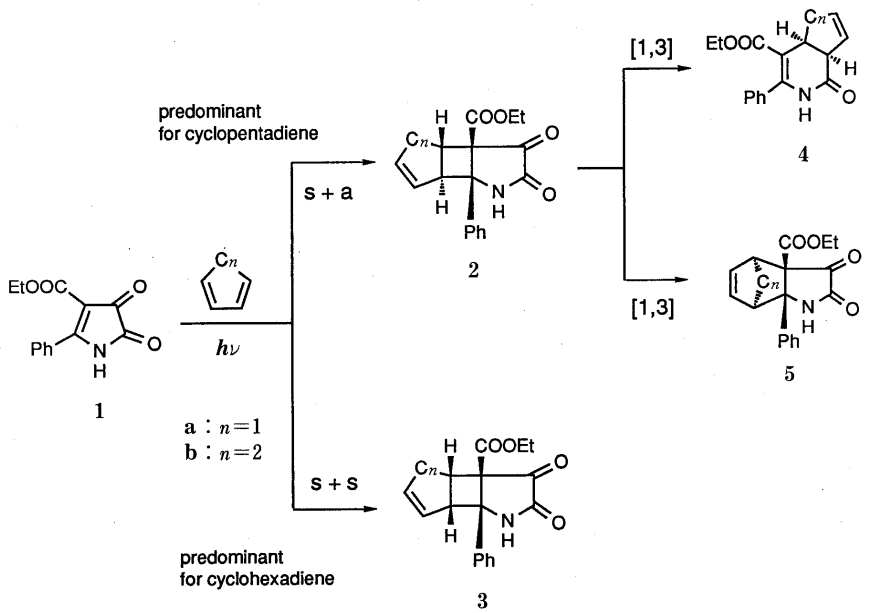


Chart 1

In this paper we describe the photocycloaddition reaction of 4,5-diethoxycarbonyl-1*H*-pyrrole-2,3-dione (**6**, 4,5-diCOOEt-dioxopyrroline) with several cycloolefins including cyclopentadiene and cyclohexadiene, providing further examples to show that a similar steric effect is an important factor influencing the polarity of the enone–olefin pair in the stereo-selection.

Results and Discussion

Cycloaddition of 4,5-DiCOOEt-dioxopyrroline to Cycloalkadienes Irradiation of a solution of **6** and cyclopentadiene in benzene with a high-pressure mercury lamp at 0 °C gave the cyclobutane **7a** and the hydroindole **8a** as mixed crystals of 1 : 3 ratio in 55% yield. Each of the adducts was obtained in a pure form by column chromatography followed by repeated crystallization. Similarly, a benzene solution of **6** and cyclohexadiene, on irradiation, gave the cyclobutane **7b** (22%) and the hydroindole **8b** (9%). Thus, cyclopentadiene gave the hydroindole as a major adduct, while cyclohexadiene gave the cyclobutane as a major one.

The structures of these photoadducts were elucidated as follows. The hydroindole **8** has the structure of a 1,4-addition product in a formal sense. Thus, we carried out the Diels–Alder (DA) reaction of **6**. Heating of **6** with cyclopentadiene in toluene at 120 °C for 2 h gave the *endo*-DA-adduct **9a** and the *exo*-DA-adduct **8a** as a 3 : 1 mixture (78%). Each of the adducts was obtained in a pure form by column chromatography and repeated crystallization. The minor DA-adduct **8a** was proved to be identical with the major photo-adduct of the dioxopyrroline **6** to cyclopentadiene. Similarly, the DA reaction of **6** with cyclohexadiene, on heating in a toluene solution at 160 °C for 1 h, gave the *exo*-DA-adduct **8b** and the *endo*-DA-adduct **9b** in a ratio of 1 : 3 (24%). The minor DA-adduct **8b** was proved to be identical with the minor photo-product from cyclohexadiene.

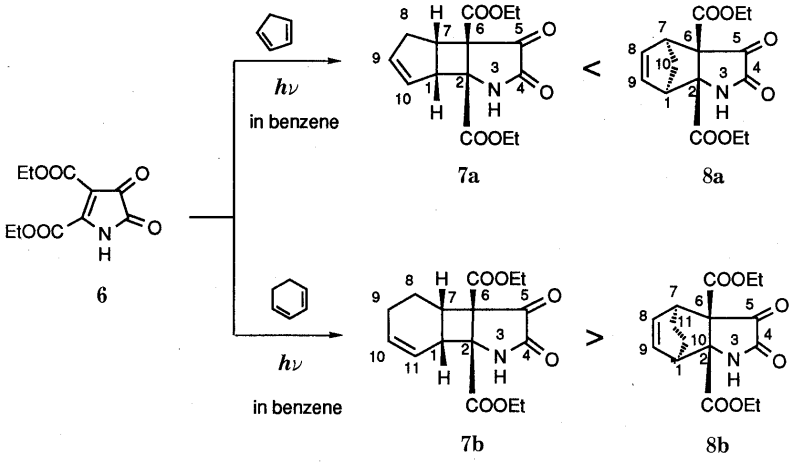
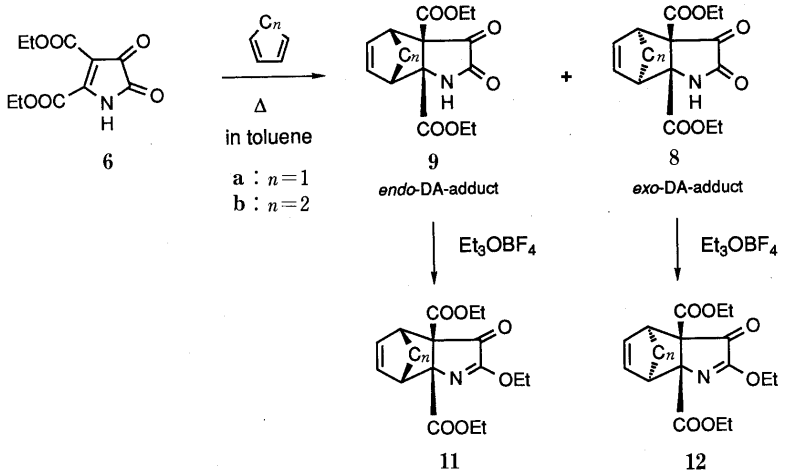


Chart 2



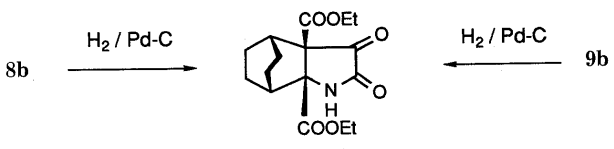


Chart 3

The structure of the DA adducts was determined as follows. Catalytic hydrogenation of **8b** and **9b** over 5% Pd–C gave the same dihydro derivative **10**, thus proving that **8b** and **9b** are the stereoisomeric hydroindoles. The structure of **9b** including the stereochemistry was unambiguously determined by an X-ray crystallographic analysis as the *endo*-adduct depicted in Fig. 1. Thus the minor DA adduct **8b** must be the *exo*-adduct.

The stereochemistry of the cyclopentadiene DA-adducts **8a** and **9a** was deduced by comparison of the spectral data with those of **8b** and **9b**. In the ^{1}H-NMR spectra the olefinic proton signals of **8b** and **9b** were significantly different, though the other spectral characteristics of the two stereoisomeric adducts were similar to each other. The olefinic protons of **8b** appeared at δ 6.22 and 6.61 as two triplets, while those of **9b** appeared at δ 6.16—6.25 as a broad multiplet of two protons. The olefinic protons of **9a** exhibited signals at δ 6.18—6.25 as a multiplet of two protons and those of **8a** at δ 6.17 and 6.61 as two triplets; thus, the stereochemistry of the methano-bridge was assigned as β in **9a** and α in **8a**.

The structures of the cyclobutanes **7a** and **7b** including the stereochemistry of the ring juncture were deduced by spectral comparison with the corresponding 2-phenyl analogs **3a** and **3b**. In particular, the chemical shifts of ring carbons in the ^{13}C-NMR spectra of **7a** and **7b** were very similar to those of **3a**[3c] and **3b**[3d] respectively, as shown in Table I. The results suggested that the adducts **7a** and **7b** have the same stereochemistry as **3a** and **3b**, thus being assigned as *cis-syn-cis*.

This assignment was supported by the following chemical transformations. Treatment of **7b** with triethyloxonium fluoroborate gave the imidate **13b** that, on pyrolysis at 300 °C, was converted into the hydroindole **12b**, though the yield was poor (4%). This compound was proved to be identical with the imidate prepared from **8b**. This result established that 7-H and 6-COOEt are in *syn*-relationship.[4]

The imidate **13a** prepared from **7a**, on pyrolysis at 200 °C, was converted into the dihydropyridone **14** in a yield of 75%. This chemical conversion was interpreted as a 1,3-shift followed by cheletropic loss of carbon monoxide from the resulting intermediate **15** (Chart 4), thus again confirming that the 7-H and the 6-COOEt are in *syn* relationship, since otherwise, the [1,3] shift would be geometrically impossible.[5]

Cycloaddition of 4,5-DiCOOEt-dioxopyrroline to Cycloalkenes Similar irradiation of a benzene solution of **6** and cyclopentene gave the cyclobutane **16** as a major adduct (27%) together with a trace of the dihydropyridone **17** (0.2%). The structure of **16** was elucidated by chemical correlation with the cyclopentadiene adduct **7a**. Catalytic hydrogenation of **7a** over 5% Pd–C gave a dihydro derivative that was identical with **16**. Thus, the stereochemistry was determined as *cis-syn-cis*. On the other hand, the minor adduct **17** was deduced to be a dihydropyridone by comparison of the spectral data with those of the phenyl

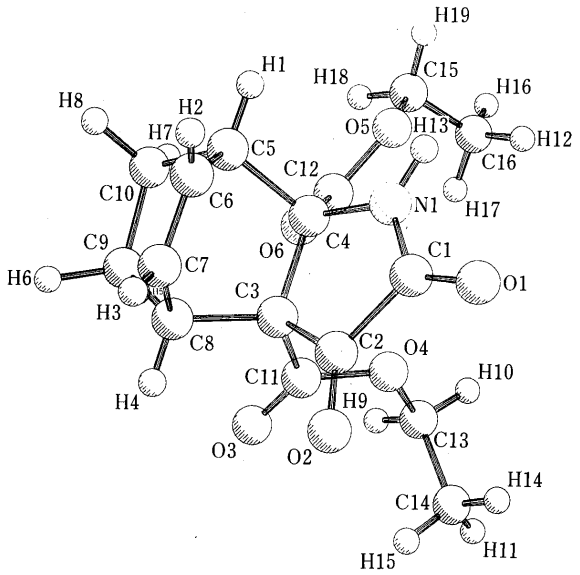


Fig. 1

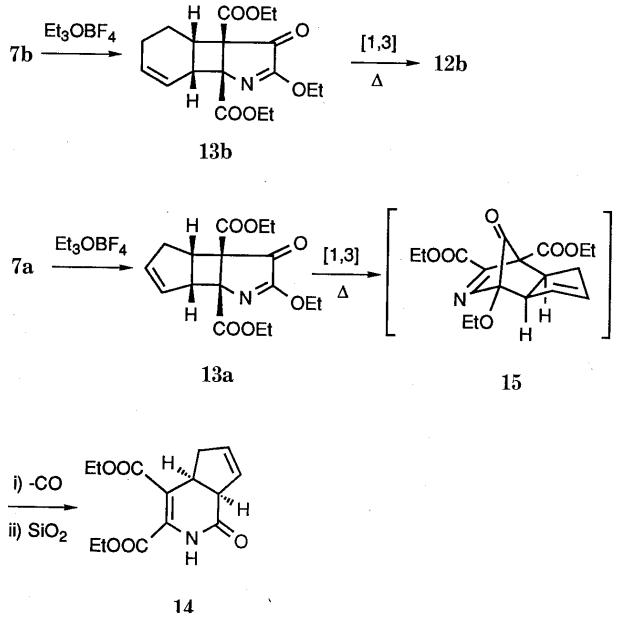


Chart 4

Table I. ^{13}C-NMR Spectral Data for Cyclobutanes **3** and **7**

Cyclobutanes	Chemical shifts of ring carbons (δ value)									
	1	2	4	5	6	7	8	9	10	11
3a[3c]	56.7	65.6	165.9	193.1	61.8	37.4	34.1	130.8[a]	137.7[a]	
7a	58.6	66.6	159.4	193.8	58.1	38.8	34.0	125.1[a]	138.5[a]	
3b[3d]	41.0	64.9	166.4	195.6	62.4	33.2	18.7	21.1	124.2[b]	132.3[b]
7b	39.0	63.4	161.7	193.0	59.0	34.9	18.4	20.8	122.8[b]	134.2[b]

a) The assignment of 9- and 10-C may be reversed. *b*) The assignment of 10- and 11-C may be reversed.

analog **4a**.[3c] Thus, the major stereochemical pathway of this cycloaddition is an s+s process, which is in sharp contrast to the case of the 4-phenyl analog, where the major stereochemical pathway is an s+a process.[3c]

Photocycloaddition of **6** to cyclohexene gave the cyclobutane **18** with *cis-syn-cis* configuration, an s+s adduct, in 15% yield as a sole product. The stereochemistry of **18** was confirmed by the fact that this compound was identical with the dihydro derivative obtained by catalytic hydrogenation of the cyclohexadiene photoadduct **7b**. Thus, the major stereochemical pathway is again an s+s process. Similar photocycloaddition of 4-COOEt-5-Ph-dioxopyrroline to cyclohexene gave no characterizable product.[3d]

Photocycloaddition of **6** to indene gave the cyclobutane **19** (15%) as a major product and a trace of the dihydropyridone **21** (0.5%). The stereochemistry of **19** was elucidated on the basis of the following evidence. In the ^{1}H-NMR spectrum of **19** the protons on the cyclobutane ring were observed to be coupled to each other with $J=7$ Hz, as in the cyclopentadiene adducts **7a** and **3a** (Fig. 2), indicating that these protons are in a *cis* relation. In the ^{13}C-NMR spectrum of **19**, the chemical shifts of cyclobutane ring carbons were very similar to those of **7a** and **3a** (Fig. 2), suggesting that they have the same stereochemistry. Treatment of **19** with triethyloxonium fluoroborate gave the imidate **22** that, on heating in xylene at 250 °C, rearranged into the dihydropyridone **21** in 10% yield. Therefore, the configuration of **19** was established as *cis-syn-cis*, since for other configurations such as *cis-anti-cis*, the 1,3-shift is geometrically impossible.[5] Thus, the major stereochemical pathway of the cycloaddition of indene is an s+s process.

Interpretation of the Stereochemical Pathway Here we discuss how these photo-adducts were formed and why the stereochemical results are different depending on the nature of the olefins or dienes. The major stereochemical results are summarized in Table II.

In the photocycloaddition of the dioxopyrroline–cycloalkadiene pair, two transition states, an *endo*-π-complex and an *exo*-π-complex, are possible. The former transition should be favored over the latter, since the two addends gain a maximum overlap of orbitals in the former complex.

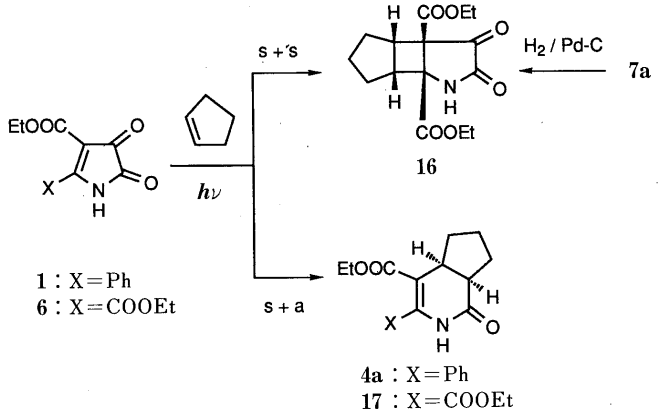


Chart 5

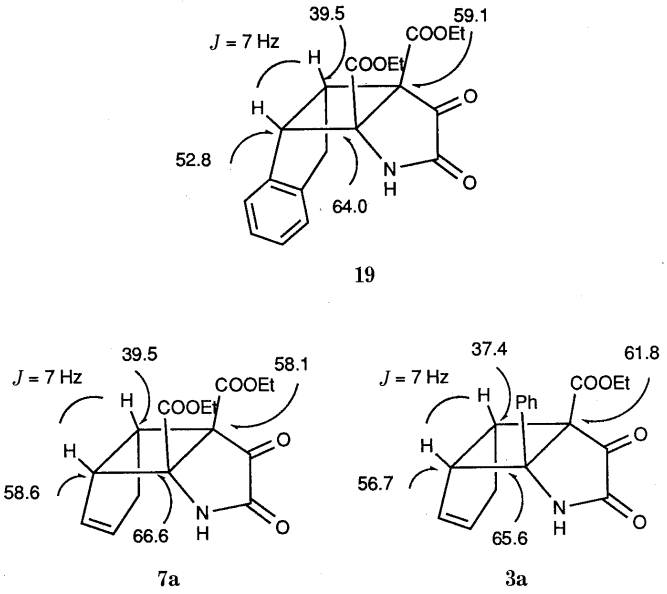


Fig. 2

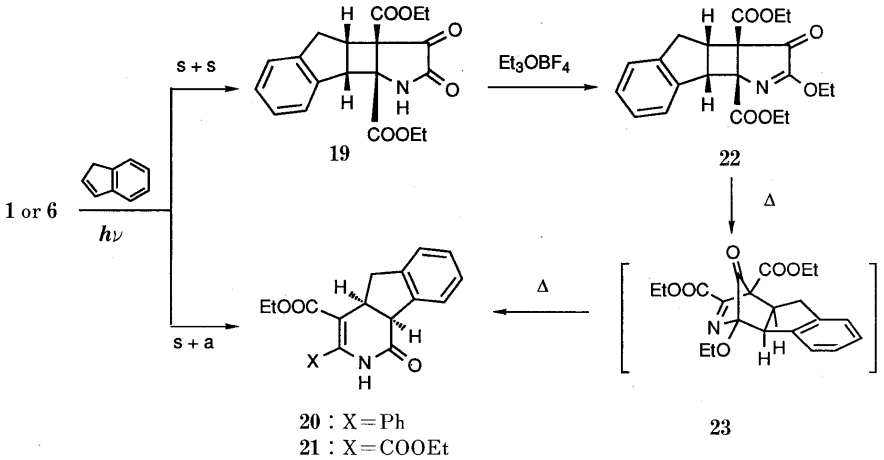
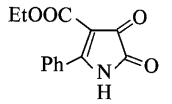
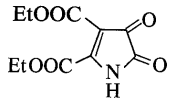
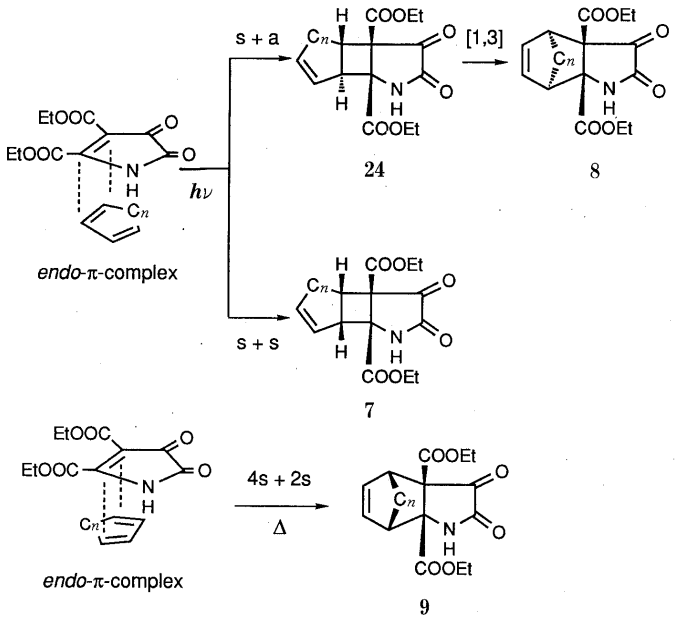


Chart 6

Table II. Major Stereochemical Results of Photocycloaddition of Dioxopyrrolines to Cycloalkadienes and Cycloalkenes

Acceptor	Donor				
					
	s+a	s+s	s+a	?	s+a
	s+a	s+s	s+s	s+s	s+s



a : $n=1$ b : $n=2$

Chart 7

It is reasonable to assume that the cyclopentadiene–4,5-diCOOEt-dioxopyrroline pair is polar, as is the 4-COOEt-5-Ph-dioxopyrroline–cyclopentadiene pair.[3c,d] In such a case the stereo-selection rule predicts that an s+a process through the *endo*-π-transition is favored over an s+s process. Since the dioxopyrroline ring is rigid, the antarafacial component in this cycloaddition is the diene, thus giving rise to the cyclobutane **24a** of *cis-syn-trans* configuration as the major adduct, accompanied with the cyclobutane of *cis-syn-cis* configuration **7a** as a minor product. The highly strained *trans*-fused cyclobutane **24a** would undergo further skeletal change: the [1,3] shift of the C_1–C_2 bond to C_9 gives the hydroindole **8a** with α-configuration of the methano bridge. This compound (**8a**) is not identical with the direct 1,4-cycloaddition product, since the [4s+2s] addition from the *endo*-π-complex produces the stereoisomer **9a**, as shown in the DA reaction.

In the case of the 4,5-diCOOEt-dioxopyrroline–cyclohexadiene pair, it is reasonable to assume that this pair is non-polar, as is the 4-COOEt-5-Ph-dioxopyrroline–cyclohexadiene pair,[3d] because the puckering effect of the ethano-bridge of cyclohexadiene increases the distance between the donor and acceptor, thus reducing the polarity of the pair. In such cases the stereo-selection rule predicts that an s+s process *via* the *endo*-π-complex is favored over an s+a process. Thus, the cyclobutane of *cis-syn-cis* configuration **7b** is formed as a major product. The minor product is the hydroindole **8b** derived from an s+a adduct, which is again different from the DA-adduct **9b**.

The photocycloaddition of 4,5-diCOOEt-dioxopyrroline to cycloalkenes gave rather unexpected results (Table II). It gave an s+s adduct as the major product, suggesting the donor–acceptor pair in the favored transition state to be non-polar. On the contrary, a similar reaction of 4-COOEt-5-Ph-dioxopyrroline with cyclopentene or indene gave the adduct derived from an s+a process as a major product, indicating that the pair in this reaction is polar.[3c] Although this change of the stereochemical result caused by the change of a phenyl to an ethoxycarbonyl group is apparently attributable to the alteration of the polarity in the donor–acceptor pair, it can not simply be explained in terms of the electronic properties of the substituent, since the COOEt group is more electron-attracting than the phenyl group. It is rather attributable to the increase of steric interaction between the donor and acceptor. As the COOEt group is bulkier than the phenyl group, the steric interaction in the favored *endo*-π-complex is larger for the diCOOEt-dioxopyrroline–cycloalkene pair than for the Ph-COOEt-dioxopyrroline–cycloalkene pair, thus increasing the distance between the donor and acceptor in the transition state of the former pair. This steric effect operates more effectively than the electronic effect does in the transition state, as discussed previously.[3d] Thus, changing the substituent on dioxopyrroline from Ph to COOEt decreases the polarity of the dioxopyrroline–cycloalkene pair causing the latter pair to be non-polar. Cyclopentadiene is almost planar, so the steric interaction in the transition state is smaller than that in the other pairs formed from cycloalkene or cyclohexadiene, and the reaction is almost unaffected by the change of the substituent from Ph to COOEt.

Thus is the first example demonstrating that a substituent on the dioxopyrroline affects the stereochemical pathway of the dioxopyrroline–olefin photocycloaddition reactions.

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were taken on a Yanagiomoto micro hot-stage melting point apparatus and are uncorrected. IR spectra were taken in Nujol mulls for solids and CH_2Cl_2 solution for gums with a Hitachi 260-10 spectrometer and are given in cm^{-1}. UV spectra were recorded in dioxane solution with a Hitachi 200-10 spectrometer 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 as an internal standard on a JEOL FX-100 spectrometer. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-D300 mass spectrometer. For column chromatography, silica gel (Mallinkrodt, CC-7) was used. Thin layer chromatography (TLC) was performed on Merck precoated silica gel 60 F_{254} plates. Medium-pressure liquid chromatography (MPLC) was performed on a Kusano CIG prepacked silica gel column. The photolysis was done by internal irradiation using a 300 W high-pressure mercury lamp (Eikosha Halos PIH 300) with a Pyrex filter. The dioxopyrroline **6** was prepared by the known method.[6]

Photocycloaddition of 6 with Cyclopentadiene A solution of **6** (3 g) and cyclopentadiene (4.3 g, 5 mol eq) in benzene (300 ml) was irradiated at 0 °C for 30 min. The reaction mixture was concentrated to dryness *in vacuo* and the residue in benzene–CH_2Cl_2 (1 : 1) was chromatographed to give a 1 : 3

mixture of **7a** and **8a** (2.08 g, 55%) as colorless crystals from Et_2O–hexane (the ratio was calculated from the intensity of the Me signal of COOEt). Fractional crystallization from Et_2O–hexane gave small amounts of pure crystals of **7a** and **8a**.

dl-(1*R**,2*R**,6*R**,7*R**)-2,6-Diethoxycarbonyl-3-azatricyclo[5.3.0^{1,7}.0^{2,6}]-dec-9-ene-4,5-dione (**7a**): Colorless prisms from Et_2O–hexane, mp 145—148 °C. IR: 1765, 1735, 1720. UV: 273 (2200). ^{1}H-NMR: 1.18 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.28 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.70 (1H, ddd, J=3, 5, 11 Hz, H-7), 3.34 (1H, ddd, J=11, 18 Hz, H-8), 3.52 (1H, m, H-1), 4.13 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.15 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.62 (1H, ddd, J=2, 3, 6 Hz, H-10), 6.08 (1H, dd, J=2, 6 Hz, H-10), 8.42 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.1 (q, $COOCH_2\underline{C}H_3$), 34.0 (t, C8), 38.8 (d, C7), 58.1 (s, C6), 58.6 (s, C1), 61.7 (t, $COO\underline{C}H_2CH_3$), 62.2 (t, $COO\underline{C}H_2CH_3$), 66.6 (s, C2), 125.1 (d, C9 or 10), 138.1 (d, C9 or 10), 159.4 (s, C4), 163.8 (s, $\underline{C}OOCH_2CH_3$), 166.0 (s, $\underline{C}OOCH_2CH_3$), 193.8 (s, C5). HRMS m/z Calcd for $C_{15}H_{17}NO_6$ (M^+): 307.1055. Found: 307.1035.

dl-(1*R**,2*S**,6*S**,7*R**)-2,6-Diethoxycarbonyl-3-azatricyclo[5.2.1.0^{2,6}]-dec-8-ene-4,5-dione (**8a**): Colorless prisms from Et_2O–hexane, mp 151—153 °C. IR: 1770, 1740, 1725. UV: 233 (4400). ^{1}H-NMR: 1.16 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.29 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.41—1.83 (2H, m, H-10), 3.11 (1H, m, H-1 or 7), 3.26—3.37 (1H, m, H-1 or 7), 4.11 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.14 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 6.13—6.21 (1H, m, H-8 or 9), 6.63—6.71 (1H, m, H-8 or 9), 8.98 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 44.3 (t, C10), 49.6 (d, C1 or 7), 52.3 (d, C1 or 7), 62.1 (t, $COO\underline{C}H_2CH_3$), 62.5 (t, $COO\underline{C}H_2CH_3$), 67.3 (s, C6), 70.9 (s, C2), 134.6 (d, C8 or 9), 138.2 (d, C8 or 9), 160.6 (s, C4), 166.3 (s, $\underline{C}OOCH_2CH_3$), 168.0 (s, $\underline{C}OOCH_2CH_3$), 194.7 (s, C5). HRMS m/z Calcd for $C_{15}H_{17}NO_6$ (M^+): 307.1054. Found: 307.1049.

Photocycloaddition of 6 with 1,3-Cyclohexadiene A solution of **6** (2.8 g) and cyclohexadiene (4.6 g, 5 mol eq) in benzene (300 ml) was irradiated at 0 °C for 60 min. The reaction mixture was concentrated to dryness *in vacuo* and the residue in CH_2Cl_2 was chromatographed. The eluate was separated by MPLC (solvent, AcOEt–hexane 1 : 1) to give **7b** (804 mg, 22%) and **8b** (333 mg, 9%).

dl-(1*R**,2*S**,6*R**,7*S**)-2,6-Diethoxycarbonyl-3-azatricyclo[5.3.0^{1,7}.0^{2,6}]-undec-10-ene-4,5-dione (**7b**): Colorless prisms from Et_2O–hexane, mp 107—109 °C. IR: 3200, 1760, 1720. UV: 264 (2600). ^{1}H-NMR: 1.19 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.33 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.60—2.06 (4H, m, H-8, H-9), 3.45—3.50 (1H, m, H-7), 3.51—3.66 (1H, m, H-1), 4.15 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.30 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.56—5.61 (1H, m, H-10 or 11), 6.07—6.18 (1H, m, H-10 or 11), 8.74 (1H, br s, NH). ^{13}C-NMR: 14.0 (q, $COOCH_2\underline{C}H_3$), 14.1 (q, $COOCH_2\underline{C}H_3$), 18.4 (t, C8), 20.8 (t, C9), 34.9 (d, C7), 39.0 (d, C1), 59.0 (s, C6), 62.4 (t, $COO\underline{C}H_2CH_3$), 62.6 (t, $COO\underline{C}H_2CH_3$), 63.4 (s, C2), 122.8 (d, C10 or 11), 134.2 (d, C10 or 11), 161.7 (s, C4), 165.7 (s, $\underline{C}OOCH_2CH_3$), 168.6 (s, $\underline{C}OOCH_2CH_3$), 193.0 (s, C5). *Anal.* Calcd for $C_{16}H_{19}NO_6$: C, 59.80; H, 5.96; N, 4.36. Found: C, 59.95; H, 6.03; N, 4.05. HRMS m/z (M^+): Calcd: 321.1212. Found: 321.1242.

dl-(1*R**,2*S**,6*S**,7*R**)-2,6-Diethoxycarbonyl-3-azatricyclo[5.2.2.0^{2,6}]-undec-8-ene-4,5-dione (**8b**): Colorless prisms from Et_2O–hexane, mp 154—157 °C. IR: 3450, 1770, 1725. UV: 237 (3200). ^{1}H-NMR: 1.13 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.28 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.30—1.83 (4H, m, H-10 and 11), 2.90—2.97 (1H, m, H-1 or 7), 3.35—3.45 (1H, m, H-1 or 7), 4.08 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.20 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 6.22 (1H, m, H-8 or 9), 6.61 (1H, t, J=7 Hz, H-8 or 9), 8.88 (1H, br s, NH). ^{13}C-NMR: 13.7 (q, $COOCH_2\underline{C}H_3$), 13.9 (q, $COOCH_2\underline{C}H_3$), 18.6 (t, C10 or 11), 19.7 (t, C10 or 11), 36.4 (d, C1 or 7), 39.3 (d, C1 or 7), 62.1 (t, $COO\underline{C}H_2CH_3$), 62.6 (t, $COO\underline{C}H_2CH_3$), 62.6 (s, C6), 68.0 (s, C2), 130.5 (d, C8), 133.5 (d, C9), 158.7 (s, C4), 166.8 (s, $\underline{C}OOCH_2CH_3$), 169.2 (s, $\underline{C}OOCH_2CH_3$), 196.4 (s, C5). *Anal.* Calcd for $C_{16}H_{19}NO_6$: C, 59.80; H, 5.96; N, 4.36. Found: C, 59.88; H, 6.01; N, 4.23. HRMS m/z (M^+): 321.1212. Found: 321.1228.

DA Reaction of 6 with Cyclopentadiene A solution of **6** (1 g) and cyclopentadiene (1.4 g, 5 mol eq) in toluene (10 ml) was heated at 120 °C for 90 min. The reaction mixture was concentrated to dryness *in vacuo* and the residue in benezene–CH_2Cl_2 (1 : 1) was chromatographed to give a 1 : 3 mixture of **8a** and **9a** (1.08 g, 78%) as colorless crystals from Et_2O–hexane (the ratio was calculated from the intensity of the Me signal of COOEt). Repeated crystallization from Et_2O–hexane gave a small amount of pure crystals of the major adduct **9a**.

dl-(1*R**,2*S**,6*S**,7*S**)-2,6-Diethoxycarbonyl-3-azatricyclo[5.2.1.0^{2,6}]-dec-8-ene-4,5-dione (**9a**): Colorless prisms from Et_2O–hexane, mp 151—153 °C. IR: 3260, 1775, 1730. UV: 264 (2600). ^{1}H-NMR: 1.18 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.34 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.83—1.92 (1H, m, H-10), 2.55—2.65 (1H, m, H-10), 3.24—3.26 (1H, m, H-1 or 7), 3.68—3.75 (1H, m, H-1 or 7), 4.15 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.28 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 6.18—6.26 (2H, m, H-8 and 9), 8.65 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 49.6 (d, C1 or 7), 50.4 (t, C10), 52.4 (d, C1 or 7), 62.4 (t, $COO\underline{C}H_2CH_3$), 62.9 (t, $COO\underline{C}H_2CH_3$), 65.3 (s, C6), 70.0 (s, C2), 136.3 (d, C8 or 9), 137.3 (d, C8 or 9), 159.8 (s, C4), 167.4 (s, $\underline{C}OOCH_2CH_3$), 166.8 (s, $\underline{C}OOCH_2CH_3$), 194.2 (s, C5). HRMS m/z Calcd for $C_{15}H_{17}NO_6$ (M^+): 307.1056. Found: 307.1088.

DA Reaction of 6 with 1,3-Cyclohexadiene A solution of **6** (1 g) and cyclohexadiene (1.7 g, 5 mol eq) in toluene (10 ml) was heated at 160 °C for 60 min. The reaction mixture was concentrated to dryness *in vacuo*. The residue in benzene was chromatographed to give a 1 : 4 mixture of **8b** and **9b** (316 mg, 24%) as colorless crystals from Et_2O–hexane (the ratio was calculated from the intensity of the Me signal of COOEt). Repeated crystallization from Et_2O–hexane gave a small amount of pure crystals of the major adduct **9b**.

dl-(1*R**,2*S**,6*S**,7*S**)-2,6-diethoxycarbonyl-3-azatricyclo[5.2.2.0^{2,6}]-undec-8-ene-4,5-dione (**9b**): Colorless prisms from Et_2O–hexane, mp 165—167 °C. IR: 3160, 1765, 1715. UV: 254 (2800). ^{1}H-NMR: 1.14 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.35 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.76—2.28 (4H, m, H-10, H-11), 2.90—2.98 (1H, m, H-1 or 7), 3.47—3.54 (1H, m, H-1 or 7), 4.09 (2H, qd, J=3, 7 Hz, $COOC\underline{H}_2CH_3$), 4.30 (2H, qd, J=2, 7 Hz, $COOC\underline{H}_2CH_3$), 6.16—6.25 (2H, m, H-8, H-9), 8.63 (1H, br s, NH). ^{13}C-NMR: 13.8 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 18.0 (t, C10 or 11), 21.8 (t, C10 or 11), 35.6 (d, C1 or 7), 40.7 (5, C1 or 7), 60.7 (d, C6), 61.9 (t, $COO\underline{C}H_2CH_3$), 62.7 (t, $COO\underline{C}H_2CH_3$), 65.8 (s, C2), 133.1 (d, C8 or 9), 133.2 (d, C8 or 9), 159.8 (s, C4), 167.3 (s, $\underline{C}OOCH_2CH_3$), 168.5 (s, $\underline{C}OOCH_2CH_3$), 194.9 (s, C5). HRMS m/z Calcd for $C_{16}H_{19}NO_6$ (M^+): 321.1212. Found: 321.1118.

Catalytic Reduction of DA-Adducts 8b and 9b A solution of **8b** (27 mg) or **9b** (65 mg) in EtOH (30 ml) was hydrogenated over 5% Pd–C (27 mg for **8b**, 65 mg for **9b**) at room temperature for 1.5 h. After removal of the catalyst by filtration, the filtrate was concentrated to dryness *in vacuo*. The residue in CH_2Cl_2 was chromatographed to give **10** (27 mg, 98% from **8b**, 62 mg, 95% from **9b**).

dl-(2*R**,6*R**)-2,6-Diethoxycarbonyl-3-azatricyclo[5.2.2.0^{2,6}]undeca-4,5-dione (**10**): Colorless prisms, mp 140—142 °C from Et_2O–hexane. IR: 3160, 1765, 1715. UV: 254 (2800). ^{1}H-NMR: 1.15 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.33 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.45—2.67 (10H, m, methine and methylene H), 4.09 (2H, qd, J=3, 7 Hz, $COOC\underline{H}_2CH_3$), 4.28 (2H, qd, J=2, 7 Hz, $COOC\underline{H}_2CH_3$), 8.40 (1H, br s, NH). ^{13}C-NMR: 13.7 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 19.9 (t), 21.2 (t), 21.7 (t), 21.9 (t), 30.1 (d, C1 or 7), 34.8 (t, C1 or 7), 59.4 (d, C6), 61.9 (t, $COO\underline{C}H_2CH_3$), 62.6 (t, $COO\underline{C}H_2CH_3$), 65.9 (s, C2), 159.4 (s, C4), 166.1 (s, $\underline{C}OOCH_2CH_3$), 168.5 (s, $\underline{C}OOCH_2CH_3$), 194.9 (s, C5). *Anal.* Calcd for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.55; N, 4.33. Found: C, 59.59; H, 6.33; N, 4.12. HRMS m/z (M^+): 323.1368. Found: 323.1368.

Imidation of the Photo- and DA-Adducts 7, 8 and 9 with Triethyloxonium Fluoroborate (General Procedure) A mixture of the photo- or DA-adduct (**7**, **8** or **9**) and a large excess of Et_3OBF_4 in CH_2Cl_2 (10 ml) was stirred overnight at room temperature. The reaction mixture was extracted with CH_2Cl_2. The extract was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in benzene was chromatographed to give the imidate (**13**, **11** or **12**).

dl-(1*R**,2*R**,6*R**,7*S**)-4-Ethoxy-2,6-diethoxycarbonyl-3-azatricyclo-[5.2.0^{1,7}.0^{2,6}]deca-3,9-dien-5-one (**13a**) (16 mg, 14%) was separated by MPLC [solvent, AcOEt–hexane (1 : 3)] of the imidates prepared from the mixed crystals of **7a** and **8a** (1 : 3) (107 mg), as a colorless gum. IR (CH_2Cl_2): 1750, 1730, 1625. UV: 245 (3400). ^{1}H-NMR: 1.20 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.39 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.51—1.93 (1H, m, H-8), 2.64—2.74 (1H, m, H-8), 3.38—3.58 (2H, m, H-1 and H-7), 4.12 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.26 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.01—6.09 (2H, m, H-8, 9). HRMS m/z Calcd for $C_{17}H_{21}NO_6$ (M^+): 335.1366. Found: 335.1343.

dl-(1*R**,2*S**,6*R**,7*S**)-4-Ethoxy-2,6-diethoxycarbonyl-3-azatricyclo-[5.2.0^{1,7}.0^{2,6}]undeca-3,10-dien-5-one (**13b**) (119 mg, 73%) was obtained from **7b** (150 mg) as a colorless gum. IR (CH_2Cl_2): 1730, 1620. UV: 246 (3300). ^{1}H-NMR: 1.19 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.31 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.44 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.65—1.91 (4H, m, H-8 and 9), 3.65 (2H, m, H-1 and 7), 4.13 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.25 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.47 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.60 (1H, m, H-10 or 11), 5.93 (1H, m, H-10 or 11).

HRMS *m/z* Calcd for $C_{18}H_{23}NO_6$ (M^+): 349.1524. Found: 349.1512.

dl-(1*R**,2*R**,6*R**,7*S**)-4-Ethoxy-2,6-diethoxycarbonyl-3-azatricyclo-[5.2.2.0^{2,6}]deca-4,8-dien-5-one (**11a**) (68 mg, 58%) was separated by MPLC [solvent, AcOEt–hexane (1 : 3)] of the imidates prepared from the mixed crystals **7a** and **8a** (1 : 3, 107 mg) as a colorless gum. IR (CH_2Cl_2): 1765, 1745, 1635. UV: 228 (4800). ^{1}H-NMR: 1.19 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.27 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.44 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.58—1.72 (2H, m, H-10), 3.15 (2H, m, H-1 and 7), 4.12 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.15 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.45 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.35 (1H, m, H-8 or 9), 6.57 (1H, m, H-8 or 9). HRMS *m/z* Calcd for $C_{17}H_{21}NO_6$ (M^+): 335.1367. Found: 335.1347.

dl-(1*R**,2*S**,6*S**,7*S**)-4-Ethoxy-2,6-diethoxycarbonyl-3-azatricyclo-[5.2.2.0^{2,6}]undeca-4,8-dien-5-one (**12a**) (7 mg, 64%) was obtained from **9a** (10 mg) as a colorless gum. IR (CH_2Cl_2): 1750, 1730, 1630. UV: 238 (3000). ^{1}H-NMR: 1.20 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.39 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.87, 2.68 (each 1H, m, H-10), 3.41 (1H, m, H-1 or 7), 3.55 (1H, m, H-1 or 7), 4.11 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.25 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.36 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.00 (1H, m, H-8 or 9), 6.10 (1H, m, H-8 or 9). HRMS *m/z* Calcd for $C_{17}H_{21}NO_6$ (M^+): 335.1366. Found: 335.1345.

dl-(1*R**,2*R**,6*R**,7*S**)-4-Ethoxy-2,6-diethoxycarbonyl-3-azatricyclo-[5.2.2.0^{2,6}]undeca-4,8-dien-5-one (**11b**) (14 mg, 37%) was obtained from **8b** (35 mg) as a colorless gum. IR (CH_2Cl_2): 1760, 1735, 1635. UV: 234 (3800). ^{1}H-NMR: 1.15 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.26 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.54 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.07—1.80 (4H, m, H-10 and 11), 3.22 (2H, m, H-1 and 7), 4.08 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.15 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.50 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 6.36—6.52 (2H, m, H-8 and 9). HRMS *m/z* Calcd for $C_{18}H_{23}NO_6$ (M^+): 349.1525. Found: 349.1518.

dl-(1*R**,2*S**,6*S**,7*S**)-4-Ethoxy-2,6-diethoxycarbonyl-3-azatricyclo-[5.2.2.0^{2,6}]undeca-4,8-dien-5-one (**12b**) (30 mg, 79%) was obtained from **9b** (35 mg) as a colorless gum. IR (CH_2Cl_2): 1765, 1735, 1635. UV: 244 (3900). ^{1}H-NMR: 1.09 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.26 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.33 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.65—2.16 (4H, m, H-10 and 11), 3.00—3.08 (1H, m, H-1 or 7), 3.44—3.50 (1H, m, H-1 or 7), 4.01 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.21 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.32 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.89—6.03 (2H, m, H-8 and 9). HRMS *m/z* Calcd for $C_{18}H_{23}NO_6$ (M^+): 349.1523. Found: 349.1515.

Pyrolysis of the Imidate 13b A solution of **13b** (140 mg) in *p*-cymene (2 ml) was heated in a sealed tube at 300 °C for 3 h. After removal of the solvent by evaporation *in vacuo*, the residue in benzene was chromatographed to give **12b** (5 mg, 4%) as a colorless gum.

Pyrolysis of the Imidate 13a A solution of **13a** (10 mg) in toluene (6 ml) was heated in a sealed tube at 200 °C for 5 h. After evaporation of the solvent to dryness *in vacuo*, the residue in benzene was chromatographed. The eluate was further purified by MPLC [solvent, AcOEt–hexane (1 : 1)] to give 3,4-diethoxycarbonyl-4a,7a-dihydrocyclopenta[3,4-*c*]pyridin-6-en-1(2*H*)-one (**14**) (6 mg, 75%) as colorless prisms from Et_2O–hexane, mp 108—111 °C. IR: 3400, 1745, 1690, 1645. UV: 282 (9900). ^{1}H-NMR: 1.33 (6H, t, J=7 Hz, $2COOCH_2C\underline{H}_3$), 2.36—3.01 (2H, m, H-5), 3.34—3.77 (2H, m, H-4a and 7a), 4.27 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.31 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.86—5.92 (2H, m, H-6 and 7), 7.54—7.63 (1H, br s, NH). HRMS *m/z* Calcd for $C_{14}H_{17}NO_5$ (M^+): 279.1106. Found: 279.1081.

X-Ray Crystallographic Analysis of 9b The reflection data were collected on a Rigaku AFC-5 four-cycle diffractometer using a graphite monochromated MoK_α in an ω–2θ scan mode at a 2θ scan speed of 4°/min for $3° < 2\theta < 55°$. Of the reflections collected, those above $3\sigma(I)$ level were used for the calculation. The structure of **9b** was solved by the direct method using MITHRIL[7] and refined by the full-matrix least-squares method with anisotropic thermal factors for non-hydrogen atoms and with isotropic ones for hydrogen atoms. The atomic parameters are listed in Table III.

Crystal Data for **9b**: Monoclinic, a=7.818(2) Å, b=13.769(3) Å, c=14.796(2) Å, β=100.91(1)°, V=1563.8(5) Å^3, D_c=1.36 g/cm^3, Z=4. Space group, $P2_1/c$. Reflections observed, 4121; reflections used for calculation, 2251. R=0.075.

Photocycloaddition of 6 to Cyclopentene A solution of **6** (3 g) and cyclopentene (4.2 g, 5 mol eq) in benzene (300 ml) was irradiated at 0 °C for 1 h. The reaction mixture was concentrated to dryness *in vacuo*. The residue in benzene–CH_2Cl_2 (1 : 1) was chromatographed and the eluate was further purified by MPLC [solvent, AcOEt–hexane (1 : 1)] to give **16** (1023 mg, 27%) and **17** (8 mg, 0.2%).

TABLE III. Positional Parameters and B_{eq} for the DA-Adduct **9b**

Atom	*x*	*y*	*z*
O1	1.0816 (4)	0.3760 (2)	0.0001 (2)
O2	1.0871 (4)	0.2116 (2)	0.1237 (2)
O3	0.7354 (4)	0.1978 (2)	0.2512 (2)
O4	0.6712 (4)	0.2775 (2)	0.1166 (2)
O5	0.6882 (4)	0.5437 (2)	0.1488 (2)
O6	0.6262 (4)	0.4284 (3)	0.2444 (2)
N1	0.9538 (4)	0.4487 (2)	0.1102 (2)
C1	1.0257 (4)	0.3761 (2)	0.0712 (2)
C2	1.0244 (5)	0.2888 (2)	0.1352 (2)
C3	0.9329 (4)	0.3177 (2)	0.2133 (2)
C4	0.9039 (4)	0.4287 (2)	0.1990 (2)
C5	1.0293 (5)	0.4822 (3)	0.2783 (2)
C6	1.2087 (6)	0.4433 (3)	0.2829 (3)
C7	1.2245 (6)	0.3495 (3)	0.3001 (3)
C8	1.0566 (5)	0.2997 (3)	0.3068 (2)
C9	0.9806 (7)	0.3479 (3)	0.3830 (3)
C10	0.9763 (7)	0.4577 (3)	0.3707 (3)
C11	0.7706 (5)	0.2572 (3)	0.1993 (3)
C12	0.7213 (5)	0.4633 (3)	0.1994 (2)
C13	0.5048 (9)	0.2287 (6)	0.0917 (6)
C14	0.521 (1)	0.1408 (6)	0.0399 (6)
C15	0.5300 (7)	0.5960 (4)	0.1531 (4)
C16	0.3875 (8)	0.5654 (5)	0.0853 (4)
H1	1.023 (5)	0.552 (3)	0.265 (3)
H2	1.297 (5)	0.479 (3)	0.276 (3)
H3	1.332 (6)	0.319 (3)	0.305 (3)
H4	1.068 (5)	0.232 (3)	0.317 (3)
H5	0.870 (5)	0.325 (3)	0.384 (3)
H6	1.060 (5)	0.324 (3)	0.452 (3)
H7	0.863 (7)	0.477 (4)	0.372 (3)
H8	1.071 (8)	0.495 (4)	0.422 (4)
H9	0.462 (8)	0.220 (5)	0.144 (5)
H10	0.418 (8)	0.269 (4)	0.048 (5)
H11	0.4101	0.1119	0.0209
H12	0.4196	0.5634	0.0269
H13	0.936 (6)	0.509 (3)	0.085 (3)
H14	0.5703	0.1558	−0.0122
H15	0.5958	0.0958	0.0781
H16	0.2915	0.6076	0.0839
H17	0.3540	0.5011	0.1008
H18	0.5030	0.5884	0.2124
H19	0.5500	0.6639	0.1432

dl-(1*R**,2*R**,6*R**,7*S**)-2,6-Diethoxycarbonyl-3-azatricyclo[3.3.0^{1,7}.0^{2,6}]-decane-4,5-dione (**16**): Colorless prisms from Et_2O–hexane, mp 139—141 °C. IR: 1760, 1720. UV: 263 (3000). ^{1}H-NMR: 1.18 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.51—1.73, 1.80—1.91 (each 3H, m, H-8, 9, and 10), 3.22 (1H, t, J=8 Hz, H-7), 3.77 (1H, t, J=8 Hz, H-1), 4.14 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.27 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 8.94 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 26.9 (t), 27.5 (t), 28.0 (t), 42.9 (d, C7), 44.3 (d, C1), 58.1 (s, C6), 62.1 (s, C2), 62.4 (t, $COO\underline{C}H_2CH_3$), 62.5 (t, $COO\underline{C}H_2CH_3$), 161.6 (s, C4), 165.4 (s, $\underline{C}OOCH_2CH_3$), 168.8 (s, $\underline{C}OOCH_2CH_3$), 192.9 (s, C5). *Anal.* Calcd for $C_{15}H_{19}NO_6$: C, 58.24; H, 6.19; N, 4.53. Found: C, 58.14; H, 6.12; N, 4.32.

dl-(4a*R**,7a*S**)-3,4-Diethoxycarbonyl-1-oxo-1,4a,5,6,7,7a-hexahydro-2*H*-cyclopenta[1,2-*c*]pyridine (**17**): Colorless prisms from Et_2O–hexane, mp 80—83 °C. IR: 1710, 1690, 1660. UV: 282 (10500). ^{1}H-NMR: 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.33 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.52—1.80, 2.05—2.29 (each 3H, m, H-5, 6, and 7), 2.90 (1H, td, J=9, 5 Hz, H-4a), 3.03 (1H, dd, J=9, 17 Hz, H-7a), 4.27 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.30 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 7.53 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 23.3 (t, C6), 29.4 (t, C5 or C7), 32.5 (t, C5 or C7), 40.9 (d, C4a), 42.8 (d, C7a), 61.4 (t, $COO\underline{C}H_2CH_3$), 62.6 (t, $COO\underline{C}H_2CH_3$), 119.3 (s, C4), 126.2 (s, C3), 161.3 (s, C1), 167.5 (s, $\underline{C}OOCH_2CH_3$), 171.3 (s, $\underline{C}OOCH_2CH_3$). HRMS *m/z* Calcd for $C_{14}H_{19}NO_5$ (M^+): 281.1260. Found: 281.1249.

Catalytic Reduction of the Cyclobutane 7a A solution of **7a** (25 mg) in EtOH (10 ml) was hydrogenated over 5% Pd–C (15 mg) at room temperature for 1 h. After removal of the catalyst by filtration, the filtrate

was concentrated to dryness *in vacuo* and the residue in CH_2Cl_2 was chromatographed to give **16** (20 mg, 80%).

Photocycloaddition of 6 to Cyclohexene A solution of **6** (2 g) and cyclopentene (3.4 g, 5 mol eq) in benzene (300 ml) was irradiated at 0 °C for 1 h. The reaction mixture was concentrated to dryness *in vacuo* and the residue in benzene–CH_2Cl_2 (1 : 1) was chromatographed. The eluate was further purified by MPLC [solvent, AcOEt–hexane (1 : 1)] to give *dl*-(1*R**,2*R**,6*R**,7*S**)-2,6-diethoxycarbonyl-3-azatricyclo[4.3.0^{1,7}.0^{2,6}]-undecane-4,5-dione (**18**) (391 mg, 15%) as colorless prisms from Et_2O–hexane, mp 89—90 °C. IR: 1760, 1720. UV: 265 (2800). ^{1}H-NMR: 1.19 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.31 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.57—1.83 (8H, m, H-8, 9, 10, 11), 3.01—3.09 (1H, m, H-7), 3.30—3.48 (1H, m, H-1), 4.13 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.20 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 8.89 (1H, br s, NH). ^{13}C-NMR: 14.0 (q, 2C, 2×$COOCH_2\underline{C}H_3$), 20.1 (t), 20.8 (t), 20.8 (t), 21.2 (t), 34.1 (d, C7), 38.6 (d, C1), 59.8 (s, C6), 62.4 (t, $COO\underline{C}H_2CH_3$), 62.5 (t, $COO\underline{C}H_2CH_3$), 63.5 (s, C2), 161.9 (s, C4), 165.5 (s, $\underline{C}OOCH_2CH_3$), 168.7 (s, $\underline{C}OOCH_2CH_3$), 193.7 (s, C5). *Anal.* Calcd for $C_{16}H_{21}NO_6$: C, 59.43; H, 6.55; N, 4.33. Found: C, 59.55; H, 6.34; N, 4.02.

Catalytic Reduction of the Cyclobutane 7b A solution of **7b** (50 mg) in EtOH (30 ml) was hydrogenated over 5% Pd–C (80 mg) at room temperature for 2 h. After removal of the catalyst and the solvent, the residue in CH_2Cl_2 was chromatographed to give **18** (40 mg, 81%) as colorless prisms from MeOH–hexane, mp 114—115 °C.

Photocycloaddition of 6 to Indene A solution of **6** (3 g) and indene (7.2 g, 5 mol eq) in benzene (300 ml) was irradiated at 0 °C for 45 min. The reaction mixture was concentrated to dryness *in vacuo* and the residue in benzene was chromatographed. The eluate was purified by MPLC [solvent, AcOEt–hexane (1 : 1)] to give *dl*-(4a*R**,9b*R**)-3,4-diethoxycarbonyl-1-oxo-1,2,4a,9b-tetrahydro-5*H*-indeno[3,2-*c*]pyridine (**21**) (21 mg, 0.5%) as colorless prisms from Et_2O–hexane, mp 119—120 °C. IR: 1720, 1690, 1660. UV: 274 (5800). ^{1}H-NMR: 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.34 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.97—3.87 (1H, m, H-5), 3.20 (1H, dd, J=8, 21 Hz, H-5), 3.70 (1H, dd, J=8, 10 Hz, H-4a), 4.10 (1H, d, J=8 Hz, H-9b), 4.30 (4H, q, J=7 Hz, 2×$COOC\underline{H}_2CH_3$), 7.22—7.26 (4H, m, H-6, 7, 8, and 9), 7.78 (1H, br s, NH). HRMS *m/z* Calcd for $C_{18}H_{19}NO_5$ (M^+): 329.1261. Found: 329.1260.

Further elution with benzene–CH_2Cl_2 (1 : 1) gave *dl*-(3a*R**,3b*S**,8b*S**,8c*R**)-2,6-diethoxycarbonyl-2,3-dioxo-1,2,3,3a,3b,4,8b,8c-octahydro-1*H*-indeno[2′,1′ : 3,4]cyclobuta[1,2-*b*]pyrrole (**19**) (643 mg, 15%) as colorless prisms from Et_2O–hexane, mp 185—187 °C. IR: 1760, 1740, 1720. UV: 260 (3300). ^{1}H-NMR: 1.20 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.35 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 3.17 (1H, dd, J=3, 5 Hz, H-4), 3.169 (1H, dd, J=3, 5 Hz, H-4), 3.95 (1H, ddd, J=3, 5, 7 Hz, H-3b), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.34 (1H, d, J=7 Hz, H-8b), 4.35 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 7.07—7.36 (4H, m, Ar-H), 8.50 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.0 (1, $COOCH_2\underline{C}H_3$), 33.6 (t, C4), 39.5 (d, C3b), 52.8 (d, C3b), 59.1 (s, C3a), 62.5 (t, $COO\underline{C}H_2CH_3$), 62.6 (t, $COO\underline{C}H_2CH_3$), 64.0 (s, C8c), 126.2 (d, Ar), 127.0 (d, Ar), 128.3 (d, Ar), 129.3 (d, Ar), 136.8 (s, Ar), 144.5 (s, Ar), 160.6 (s, C2), 165.2 (s, $\underline{C}OOCH_2CH_3$), 168.4 (s, $\underline{C}OOCH_2CH_3$), 190.9 (s, C3). *Anal.* Calcd for $C_{19}H_{19}NO_6$: C, 63.86; H, 5.36; N, 3.92. Found: C, 63.72; H, 5.23; N, 3.88. HRMS *m/z* (M^+): 357.1168. Found: 357.1188.

Imidation of the Cyclobutane 19 with Triethyloxonium Fluoroborate A mixture of **19** (200 mg) and a large excess of Et_3OBF_4 in CH_2Cl_2 (10 ml) was stirred overnight at room temperature. The reaction mixture was extracted with CH_2Cl_2. The extract was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in benzene was chromatographed to give *dl*-(1*R**,2*S**,6*S**,7*R**)-2-ethoxy-3a,8c-diethoxycarbonyl-3-oxo-3,3a,3b,4,8b,8c-hexahydro-1*H*-indeno[2′,1′ : 3,4]cyclobuta[1,2-*b*]pyrrole (**22**) (212 mg, 98%) as a colorless gum. IR: 1750, 1730, 1620. ^{1}H-NMR: 1.12 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.19 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.36 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 3.03—3.09 (2H, m, H-4), 3.22—3.28 (1H, m, H-3b), 4.07 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.14 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.33 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.63 (1H, d, J=7 Hz, H-8b), 7.14—7.36 (4H, m, Ar-H).

Pyrolysis of the Imidate 22 A solution of **22** (190 mg) in xylene (3 ml) was heated at 250 °C for 48 h in a sealed tube. After evaporation of the solvent *in vacuo*, the residue in CH_2Cl_2 was chromatographed. The eluate was purified by PTLC [solvent, AcOEt–hexane (1 : 1)] to give **21** (17 mg, 10%) as a colorless gum.

References and Notes

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