Dioxopyrrolines. XLVI.[1] [2+2] Photocycloaddition of 4-Ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione to Six-Membered Cycloolefins: Effect of Ring Size on Stereochemical Pathways

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Photocycloaddition reaction of 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione (1) with cyclohexadiene and dihydropyran gave the *cis*-fused cyclobutane 5b and the *trans*-fused cyclobutane 6b as major adducts, respectively. The structures including stereochemistry were established by X-ray crystallographic analysis.

The results for these systems markedly contrast with those for the photocycloaddition of 1 to five-membered cycloolefins, cyclopentadiene and dihydrofuran, which yield the adducts with skeletal rearrangements. The difference of product depending on the ring size can be related to the difference in the stereochemical pathways. The distance between donor and acceptor is suggested to be an important factor determining the polarity of the donor–acceptor pair and, therefore, the stereochemistry of the photocycloaddition.

Keywords photocycloaddition; 1*H*-pyrrole-2,3-dione; dioxopyrroline; cyclohexadiene; dihydropyran; cyclobutane; stereochemistry; polarity; donor–acceptor interaction

Recently, we showed that the stereochemical results in the photocycloaddition reaction of 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione (**1**, dioxopyrroline) to olefins leading to cyclobutanes with the head-to-tail (HT) regiochemistry changed depending on the electronic properties of the olefins.[2] Olefins with a strong electron-donating substituent (strong electron donors) give products in which the configuration of the olefin is retained (s+s product, that is, *endo*), while those with a weak electron-donating substituent (weak electron donors) give the products in which the configuration of the olefins is inverted (s+a product, that is, *exo*).[3] The results could be explained by the stereoselection rule.[3]

On the other hand, five membered cycloolefins gave a series of products of completely different structures. For example, cyclopentadiene yielded the dihydropyridone **3a** and the hydroindole **4a** as the major products.[1,4] Dihydrofuran gave the dihydropyridone **7a** and the difurano derivative **8a**.[5] The formation of these products, however, was explicable in terms of skeletal rearrangement of the highly strained cyclobutanes **2a** and **10a**, which are also expected from the stereoselection rule, respectively.

In contrast to cyclopentene derivatives, photocycloaddition of dioxopyrroline (**1**) to cycloolefins with a six-membered ring gave rather contradictory results: the major products were the cyclobutane of *cis-syn-cis* configuration **5b** from cyclohexadiene and that of *cis-syn-trans* configuration **6b** from dihydropyran. This paper deals with this case in detail.

Results and Discussion

Irradiation of a solution of **1** and cyclohexadiene in dimethoxyethane with a high-pressure mercury lamp gave the cyclobutane **5b**, the dihydropyridone **3b**, and the hydroindole **4b** in yields of 28%, 1%, and 2% respectively. In contrast, cyclohexene on similar irradiation did not give any adduct. The structures of these photoadducts were deduced from their spectral similarity with the corresponding cyclopentadiene adducts **3a**—**5a**. The ultraviolet (UV) spectrum of **3b** showed the absorption band at 286 nm characteristic of the dihydropyridone moiety. The adduct **4b** showed a very similar ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum to that of **4a** except for the presence of the additional signals of one methylene group, suggesting

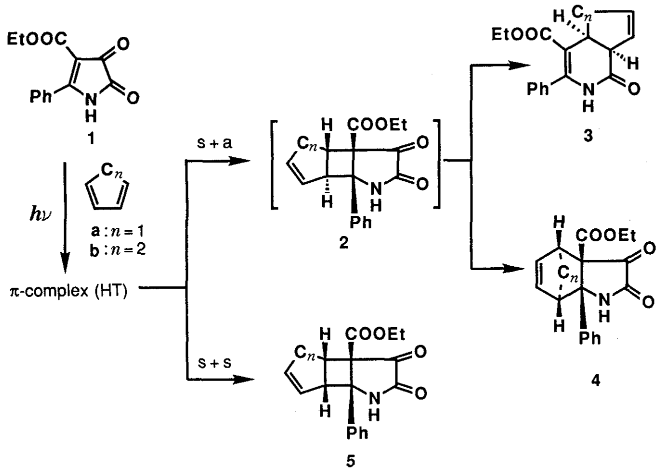

Chart 1

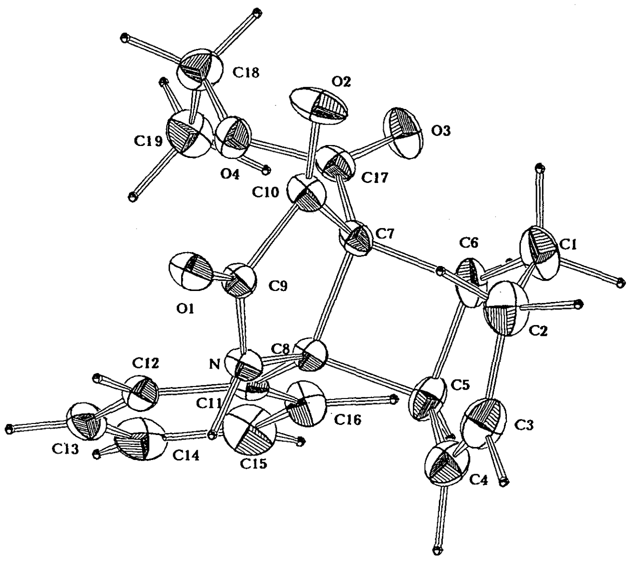

Fig. 1

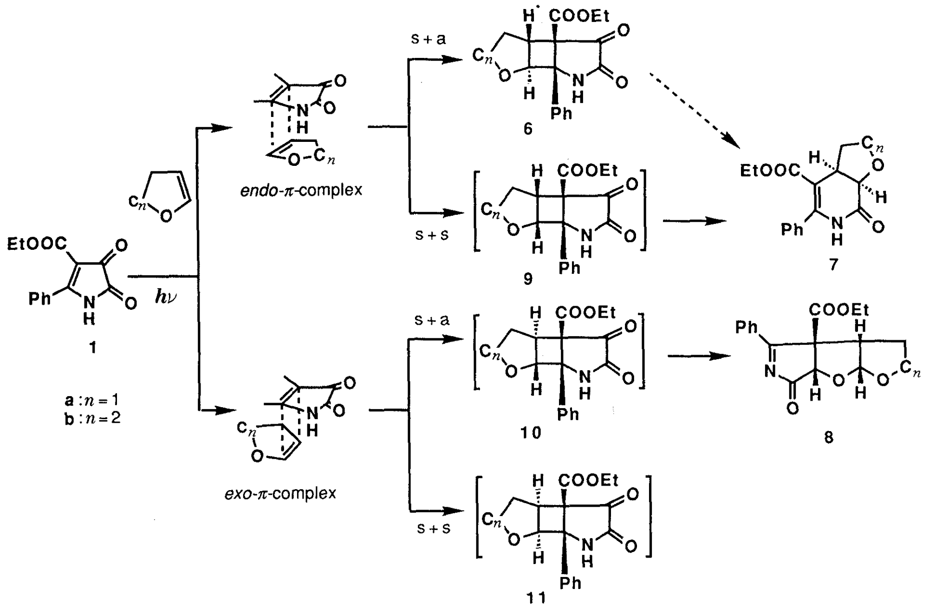

Chart 2

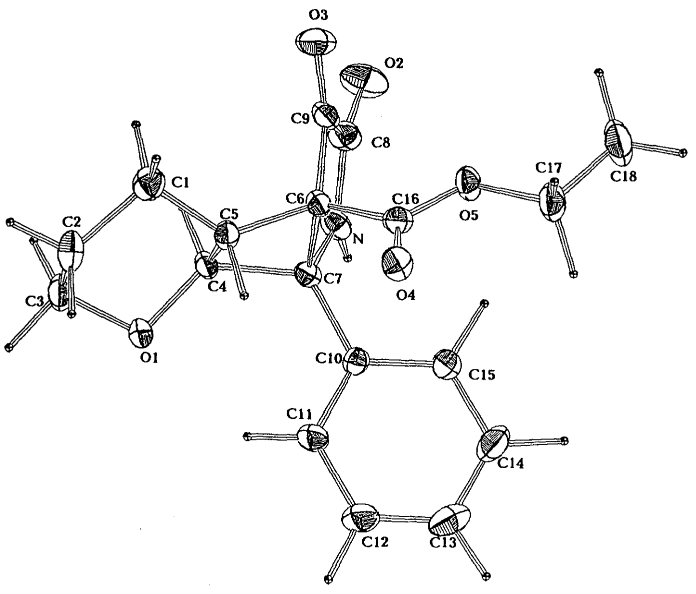

Fig. 2

Table I. The Stereochemical Pathways of the Photocycloaddition Reaction of **1** to Cycloolefins

Cycloolefins	Stereochemical pathways % (products)$^{a)}$			
	endo-π-Pathways		*exo*-π-Pathways$^{b)}$	
	[s+s]	[s+a]	[s+s]	[s+a]
Cyclopentadiene	10 (**5a**)	41 {24 (**3a**) 17 (**4a**)}		
Cyclohexadiene	28 (**5b**)	3 {1 (**3b**) 2 (**4b**)}		
Dihydrofuran	24 (**7a**)$^{c)}$	—	—	9 (**8a**)
Dihydropyran	—	19 (**6b**)	—	4 (**8b**)

a) All products have HT regiochemistry in cycloadditions. *b*) In cyclohexadiene (cyclopentadiene) *exo*- and *endo*-pathways are hardly distinguishable because if we slide one components slightly, the former array gives the latter array. On the other hand in dihydropyran (dihydrofuran) the two pathways are clearly distinguishable. *c*) See reference 6.

that this is the hydroindole. The stereochemistry of the ethano bridge between C_4 and C_7 in **4b** was assigned by analogy with that of **4a**. The major adduct **5b** showed C-13 nuclear magnetic resonance (^{13}C-NMR) signals due to two tertiary carbons at δ 33.2 and 41.0, suggesting that it contains a cyclobutane moiety. The structure **5b** including the stereochemistry was unambigously established by X-ray crystallographic analysis as the cyclobutane with *cis-syn-cis* configuration (Fig. 1).

The photocycloaddition reaction of **1** with dihydropyran under a similar conditions gave the cyclobutane **6b** and the furanopyrano derivative **8b** in yields of 19% and 4%, respectively. The dihydropyridone **7b** was not detected in the reaction mixture. The structure and stereochemistry of **6b** were also unambigously determined by X-ray analysis (*trans*-fused cyclobutane in the olefin component), as depicted in Fig. 2. The other adduct **8b** exhibited spectral characteristics attributable to the acylimino moiety [strong UV absorption at 280 nm and two low ^{13}C-NMR signals at 189.4 and 191.8]. These and other spectral features are very similar to those of the dihydrofuran adduct **8a**,[5] thus proving that **8b** is a furanopyrano derivative.

The results together with those of photocycloaddition of **1** to cyclopentadiene[1,4] and to dihydrofuran[5] (Table I) revealed that the product ratios varied depending on the ring size of the olefin components. Six-membered olefins afforded the cyclobutanes as a major product, while five-membered olefins mainly formed cycloadducts with skeletal changes. The Table I clearly demonstrates that this difference in product distribution between the five- and six-membered cycloolefins may originate from the change in the stereochemical pathways. The stereochemical pathway of their formation is considered to be as shown in Charts 1 and 2, as already discussed for cyclopentadiene[1] and dihydrofuran.[5] Cyclohexadiene adds to **1** preferentially in an s+s manner *via* the *endo*-π-complex of HT orientation, while cycloaddition of cyclopentadiene proceeds mainly in an s+a manner. Dihydropyran adds to **1** preferentially in an s+a manner, while dihydrofuran mainly adds in an s+s manner.[6]

The stereochemical results obtained from the six-membered cycloolefins appear to be inconsistent with the stereo-selection rule of enone–olefin photocycloaddition recently proposed by us.[3] If the dioxopyrroline–cyclohexadiene pair is polar, as is the dioxopyrroline–cyclopentadiene pair, the rule predicts that the addition should proceed preferentially in an s+a manner. On the other hand, if we assume that the dioxopyrroline–dihydropyran pair is ver polar as is the dioxopyrroline–ethoxyethylene pair and that they overlap in an *endo* manner in the transition state, the rule also predicts that the cyclobutane with a *cis-syn-cis* stereochemistry would be formed as a result of an s+s addition.

The above inconsistency does not necessarily invalidate our stereoselection rule, but instead rather implies the importance of another factor, *i.e.* steric effect, in addition to the polar effect in the stereoselection. We have already pointed out that the most important process of stereoselection in polar 2+2 photocycloaddition lies in the bond formation in the excited π-complex.[1] The polarity of the donor–acceptor pair in the excited state controls whether the final bond formation occurs with retention (suprafacially) or with inversion (antarafacially).[3] On the other hand, our basic assumption is that there are stereochemically different plural (favored and less favored) transition complexes constructed from the two reactants. Each of them does not necessarily have the same polarity, because the distance between the two partially charged components in each pair may not be equal. Generally, the attractive intermolecular energy between two molecules, such as dipole–dipole interaction, varies inversely by the sixth power of the distance. Thus, a small change in the distance will be reflected in the polarity (the magnitude of donor–acceptor interaction) as a considerable change. These considerations indicate that the steric effect must also be an important factor in evaluation of the polarity in the excited state. This may also be the reason why the stereoselection differs in favored and less favored transitions.[3]

If we assume that cyclohexadiene and cyclopentadiene have nearly equal contributions as electron donors, their interactions with the acceptor, dioxopyrroline, in excited π-complexes (even if they have the same shapes) are apparently different, since cyclohexadiene is puckered and is bulkier than cyclopentadiene. The distance between the donor and acceptor molecules is larger in the former complex (Chart 3). This effect decreases the polarity of the former pair, and, in other words, increases the non-polar charactor, in which the normal s+s photocycloaddition process predominates.

A similar argument can be applied to dioxopyrroline–dihydrofuran *vs.* dioxopyrroline–dihydropyran pairs. The steric effect in the latter pair in the transition state decreases its very polar character, thus changing the reaction path from an s+s to an s+a.

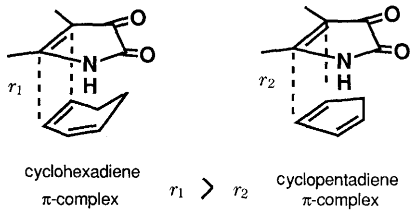

Chart 3

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were taken on a Yanagimoto micro hot-stage melting point

TABLE II. Atomic Parameters of **5b**

Atom	x	y	z	B_{eq}/B_{iso}
O1	3920 (2)	1895 (2)	3155 (2)	3.6
O2	3616 (3)	946 (2)	1254 (3)	4.5
O3	3006 (2)	2363 (3)	−1139 (2)	4.3
O4	2367 (2)	2405 (3)	210 (2)	3.4
N	3949 (2)	3172 (3)	2132 (3)	2.7
C1	5130 (4)	1820 (5)	232 (5)	5.0
C2	5558 (4)	1797 (4)	1301 (5)	5.0
C3	5791 (3)	2738 (5)	1690 (4)	4.8
C4	5398 (3)	3502 (4)	1405 (5)	4.5
C5	4692 (3)	3503 (4)	648 (4)	3.5
C6	4517 (3)	2580 (4)	65 (4)	3.7
C7	3731 (3)	2481 (3)	507 (3)	2.5
C8	3884 (3)	3435 (3)	1074 (3)	2.4
C9	3872 (3)	2274 (3)	2335 (4)	2.7
C10	3716 (3)	1765 (3)	1332 (4)	2.9
C11	3299 (3)	4212 (3)	833 (4)	2.7
C12	2764 (3)	4436 (4)	1492 (4)	3.1
C13	2233 (3)	5149 (4)	1261 (4)	3.9
C14	2213 (3)	5620 (4)	371 (5)	4.7
C15	2736 (4)	5391 (4)	−298 (5)	5.0
C16	3285 (3)	4691 (4)	−72 (4)	3.7
C17	3002 (3)	2409 (3)	−247 (4)	3.0
C18	1614 (3)	2376 (4)	−421 (4)	4.2
C19	1396 (4)	3314 (4)	−849 (5)	4.6

$B_{eq}=\frac{4}{3}\sum_i\sum_j\beta_{ij}\mathbf{a}_i\mathbf{a}_j$

Positional parameters are multiplied by ×10⁴. Thermal parameters are given by the equivalent temperature factors (Å²).

TABLE III. Bond Lengths (Å) of **5b**

Atoms	Distance (Å)
O1–C9	1.226 (5)
O2–C10	1.196 (5)
O3–C17	1.203 (5)
O4–C17	1.324 (6)
O4–C18	1.463 (6)
N–C8	1.465 (5)
N–C9	1.334 (6)
C1–C2	1.535 (8)
C1–C6	1.521 (8)
C2–C3	1.492 (9)
C3–C4	1.325 (8)
C4–C5	1.491 (7)
C5–C6	1.557 (7)
C5–C8	1.576 (7)
C6–C7	1.555 (7)
C7–C8	1.581 (6)
C7–C10	1.520 (6)
C7–C17	1.519 (6)
C8–C11	1.517 (6)
C9–C10	1.532 (6)
C11–C12	1.397 (7)
C11–C16	1.399 (7)
C12–C13	1.388 (7)
C13–C14	1.375 (8)
C14–C15	1.391 (9)
C15–C16	1.394 (8)
C18–C19	1.500 (8)

Standard deviations are in parentheses.

apparatus, and are uncorrected. Infrared (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} (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. High-resolution mass spectra (MS) were recorded on a JEOL JMS-D300 mass spectrometer. Thin layer chromatography (TLC) was performed on precoated Silica gel 60 F_{254} plates (Merck). Silica gel used for column chromatography was Wako-gel C-200. The photolysis solution was irradiated internally using a 300 W high-pressure mercury lamp (Eikosha Halos PIH 300) with a Pyrex filter.

The Photocycloaddition of Dioxopyrroline 1 to Cyclohexadiene A solution of **1**$^{7)}$ (5 g, 20 mmol) and cyclohexadiene (8.15 g, 100 mmol) in dimethoxyethane (300 ml) was irradiated at 0 °C for 1.5 h. After evaporation of the solvent, the residue was dissolved in benzene and chromatographed over SiO_2. Elution with benzene–CH_2Cl_2 (1 : 1) and CH_2Cl_2, and crystallization of the product from CH_2Cl_2–Et_2O gave 6-ethoxycarbonyl-2-phenyl-3-azatricyclo[5.4.0.^{1,7}0^{2,6}]undec-10-ene-4,5-dione (**5b**, 1.90 g, 28%) as colorless prisms, mp 178—180 °C. IR: 3150—3050, 1760, 1710, 1680. ^{1}H-NMR: 0.71 (3H, t, J=7 Hz, $\mathrm{COOCH_2C\underline{H}_3}$), 1.84—1.99 (4H, m, C_8-H and C_9-H), 3.6—3.8 (4H, m, $\mathrm{COOC\underline{H}_2CH_3}$ overlapped with C_1-H and C_7), 5.80 and 6.10 (each 1H, m, C_{10}-H and C_{11}-H), 7.3—7.6 (5H, m, ArH). ^{13}C-NMR: 13.4 (q, $\mathrm{COOCH_2\underline{C}H_3}$), 18.7 (t, C_8), 21.1 (t, C_9), 33.2 (d, C_7), 41.0 (d, C_1), 61.8 (t, $\mathrm{COO\underline{C}H_2CH_3}$), 62.4 (s, C_6), 64.9 (s, C_2), 124.2 (d, C_{10} or C_{11}), 125.6 (d, 2C, Ph), 128.5 (d, Ph), 128.7 (d, 2C, Ph), 132.3 (d, C_{10} or C_{11}), 137.1 (s, Ph), 163.8 (s, C_4), 166.4 (s, $\mathrm{\underline{C}OOCH_2CH_3}$), 195.6 (s, C_5). *Anal.* Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 69.86; H, 6.08; N, 4.14.

The mother liquor was dissolved in hexane and chromatographed over SiO_2. Elution with hexane–benzene (3 : 2) and crystallization of the product from Et_2O–hexane gave (4aR*, 8aS*)-4-ethoxycarbonyl-3-phenyl-1,2,4a,5,6,8a-hexahydroisoquinolin-1-one (**3b**, 80 mg, 1%) as

TABLE IV. Bond Angles (°) of **5b**

Atoms	Angle (°)
C17–O4–C18	117.3 (3)
C8–N–C9	117.0 (3)
C2–C1–C6	113.6 (5)
C1–C2–C3	112.8 (5)
C2–C3–C4	123.2 (5)
C3–C4–C5	123.1 (5)
C4–C5–C6	115.8 (4)
C4–C5–C8	115.9 (4)
C6–C5–C8	90.3 (3)
C1–C6–C5	116.9 (4)
C1–C6–C7	120.2 (4)
C5–C6–C7	90.6 (3)
C6–C7–C8	90.2 (3)
C6–C7–C10	115.9 (3)
C6–C7–C17	116.1 (3)
C8–C7–C10	104.8 (3)
C8–C7–C17	117.3 (3)
C10–C7–C17	110.8 (3)
N–C8–C5	113.9 (3)
N–C8–C7	103.4 (3)
N–C8–C11	111.6 (3)
C5–C8–C7	88.9 (3)
C5–C8–C11	118.2 (3)
C7–C8–C11	118.2 (3)
O1–C9–N	128.3 (4)
O1–C9–C10	124.5 (4)
N–C9–C10	107.2 (3)
O2–C10–C7	128.4 (4)
O2–C10–C9	124.0 (4)
C7–C10–C9	107.6 (3)
C8–C11–C12	120.7 (4)
C8–C11–C16	119.3 (4)
C12–C11–C16	119.9 (4)
C11–C12–C13	120.0 (4)
C12–C13–C14	120.4 (5)
C13–C14–C15	120.0 (5)
C14–C15–C16	120.6 (5)
C11–C16–C15	119.0 (5)
O3–C17–O4	124.8 (4)
O3–C17–C7	124.4 (4)
O4–C17–C7	110.8 (3)
O4–C18–C19	111.2 (4)

TABLE V. Atomic Parameters of **6b**

Atom	x	y	z	B_{eq}/B_{iso}
O1	4550 (3)	712 (3)	7665 (4)	2.7
O2	2684 (4)	−1785 (4)	10681 (6)	5.1
O3	1408 (3)	−821 (4)	8052 (5)	4.0
O4	1827 (3)	2660 (3)	8401 (5)	3.3
O5	1598 (3)	1399 (3)	9993 (5)	3.1
N	3588 (3)	−248 (4)	10479 (5)	2.7
C1	2526 (5)	514 (6)	5734 (7)	3.4
C2	3391 (5)	737 (7)	5178 (7)	4.0
C3	4332 (5)	304 (6)	6187 (7)	3.7
C4	3751 (4)	403 (5)	8101 (6)	2.4
C5	2854 (4)	979 (5)	7244 (6)	2.4
C6	2484 (4)	785 (5)	8538 (6)	2.2
C7	3568 (4)	717 (5)	9538 (6)	2.2
C8	2817 (5)	−916 (5)	10098 (7)	3.2
C9	2113 (4)	−371 (5)	8774 (7)	2.7
C10	3977 (4)	1764 (5)	10357 (6)	2.3
C11	4539 (5)	2504 (5)	9881 (7)	3.2
C12	4877 (5)	3506 (6)	10637 (8)	4.0
C13	4636 (5)	3768 (6)	11856 (9)	4.6
C14	4066 (5)	3033 (7)	12354 (8)	4.7
C15	3743 (5)	2030 (6)	11615 (7)	3.4
C16	1926 (4)	1734 (5)	8928 (7)	2.8
C17	1117 (5)	2271 (7)	10595 (8)	4.0
C18	680 (6)	1667 (7)	11565 (9)	5.5

$$B_{eq}=\frac{4}{3}\sum_i\sum_j \beta_{ij}\boldsymbol{a}_i\boldsymbol{a}_j$$

Positional parameters are multiplied by $\times 10^4$. Thermal parameters are given by the equivalent temperature factors (Å^2).

TABLE VI. Bond Lengths (Å) of **6b**

Atoms	Distance (Å)
O1–C3	1.465 (8)
O1–C4	1.430 (8)
O2–C8	1.220 (8)
O3–C9	1.199 (6)
O4–C16	1.201 (7)
O5–C16	1.339 (8)
O5–C17	1.476 (9)
N–C7	1.461 (7)
N–C8	1.352 (8)
C1–C2	1.568 (11)
C1–C5	1.513 (8)
C2–C3	1.539 (9)
C4–C5	1.509 (7)
C4–C7	1.558 (9)
C5–C6	1.545 (9)
C6–C7	1.619 (7)
C6–C9	1.518 (8)
C6–C16	1.514 (8)
C7–C10	1.500 (7)
C8–C9	1.540 (8)
C10–C11	1.387 (9)
C10–C15	1.413 (9)
C11–C12	1.408 (9)
C12–C13	1.382 (12)
C13–C14	1.403 (12)
C14–C15	1.396 (10)
C17–C18	1.487 (13)

Standard deviations are in parenthesis.

Table VII. Bond Angles (°) of **6b**

Atoms	Angle (°)
C1–C2–C3	114.1 (5)
O1–C3–C2	114.2 (6)
O1–C4–C5	113.4 (5)
O1–C4–C7	126.8 (4)
C5–C4–C7	91.5 (4)
C1–C5–C4	110.4 (5)
C1–C5–C6	131.2 (5)
C4–C5–C6	87.4 (4)
C5–C6–C7	87.9 (4)
C5–C6–C9	119.8 (5)
C5–C6–C16	117.3 (4)
C7–C6–C9	101.9 (4)
C7–C6–C16	114.2 (4)
C9–C6–C16	111.9 (5)
N–C7–C4	114.1 (4)
N–C7–C6	104.2 (4)
N–C7–C10	112.3 (4)
C4–C7–C6	83.2 (3)
C4–C7–C10	121.7 (5)
C6–C7–C10	116.9 (4)
O2–C8–N	127.4 (5)
O2–C8–C9	125.5 (5)
N–C8–C9	107.1 (5)
O3–C9–C6	127.2 (5)
O3–C9–C8	124.2 (5)
C6–C9–C8	108.5 (4)
C7–C10–C11	121.9 (5)
C7–C10–C15	118.8 (5)
C11–C10–C15	119.2 (5)
C10–C11–C12	120.7 (6)
C11–C12–C13	119.8 (7)
C12–C13–C14	120.4 (6)
C13–C14–C15	119.7 (7)
C10–C15–C14	120.2 (6)
O4–C16–O5	125.3 (6)
O4–C16–C6	124.9 (6)
O5–C16–C6	109.7 (4)
O5–C17–C18	106.3 (6)

Standard deviations are in parenthesis.

colorless prisms, mp 144—145 °C. IR: 3200, 1670, 1640. UV: 226 (10000), 286 (10200). ^{1}H-NMR: 0.92 (3H, t, $J=7$ Hz, $COOCH_2C\underline{H}_3$), 1.6—2.3 (4H, m, 2×CH_2), 3.0—3.4 (2H, m, 2×CH), 3.96 (2H, q, $J=7$ Hz, $COOC\underline{H}_2CH_3$), 6.00 (2H, br s, olefinic H), 7.4 (5H, br s, ArH). HRMS *m/z*: Calcd for $C_{18}H_{19}NO_3$: 297.1365. Found: 297.1378.

Further elution with CH_2Cl_2 and crystallization of the product from CH_2Cl_2–Et_2O gave (3a*S**, 4*S**, 7*S**, 7a*S**)-3a-ethoxycarbonyl-7a-phenyl-2,3,3a,4,7,7a-hexahydro-4,7(ethano)-indole-2,3-dione (**4b**, 160 mg, 2%) as colorless prisms, mp 188—190 °C. IR: 3150—3050, 1760, 1740, 1710, 1680. ^{1}H-NMR: 0.63 (3H, t, $J=7$ Hz, $COOCH_2C\underline{H}_3$), 1.1—1.4 (4H, 2×CH_2), 3.0—3.8 (4H, m, $COOC\underline{H}_2CH_3$ overlapped with C_4 and C_7-H), 6.64 (2H, m, C_5 and C_6-H), 7.23—7.54 (5H, m, ArH). ^{13}C-NMR: 13.0 (q, $COOCH_2\underline{C}H_3$), 19.5 (t, C_8 or C_9), 21.0 (t, C_8 or C_9), 38.3 (d, C_4 or C_7), 41.9 (d, C_4 or C_7), 66.6 (s, C_{3a}), 68.0 (s, C_{7a}), 126.0 (d, 2C, Ph), 127.8 (d, Ph), 128.2 (d, 2C, Ph), 132.3 (d, C_5 or C_6), 133.9 (d, C_5 or C_6), 141.4 (s, Ph), 160.2 (s, C_2), 167.8 (s, $\underline{C}OOCH_2CH_3$), 198.7 (s, C_3). *Anal.* Calcd for $C_{19}H_{19}NO_4 \cdot 1/2\,H_2O$: C, 78.25; H, 6.03; N, 4.19. Found: C, 68.77; H, 6.17; N, 3.92. HRMS *m/z*: M^+ Calcd for $C_{19}H_{19}NO_4$: 325.1314. Found: 325.1332.

The Photocycloaddition of 1 to 2,3-Dihydropyran A solution of **1** (2 g, 8 mmol) and 2,3-dihydropyran (4.8 g, 56 mmol) in dimethoxyethane (300 ml) was irradiated for 1 h at 0 °C. After removal of the solvent, the residue in benzene was chromatographed over silica gel. Elution with benzene and crystallization of the product from CH_2Cl_2–Et_2O gave (1*S**, 3*R**, 8*S**, 9*R**)-9-ethoxycarbonyl-10-phenyl-2,4-dioxa-11-azatricyclo[7.3.0.^{1,9}0^{3,8}]dodec-10-en-2-one (**8b**, 105 mg, 4%) as colorless prisms, mp 173—174 °C. IR: 1750, 1720. UV: 280 (20000). ^{1}H-NMR: 1.03 (3H, t, $J=7$ Hz, $COOCH_2C\underline{H}_3$), 1.2—1.8 (4H, m, C_6-H and C_7-H), 3.15 (1H, m, C_8-H), 3.7 (2H, m, C_5-H), 4.16 (2H, q, $J=7$ Hz, $COOC\underline{H}_2CH_3$), 4.46 (1H, s, C_1-H), 5.50 (1H, d, $J=3.4$ Hz, C_3-H), 7.5 (3H, m, Ar-H), 8.0 (2H, m, Ar-H). ^{13}C-NMR: 13.7 (q, $COOCH_2\underline{C}H_3$), 21.1 and 22.1 (each t, C_6 and C_7), 39.4 (d, C_8), 62.0 (t, C_5), 66.9 (s, C_9), 67.7 (t, $COOCH_2CH_3$), 81.1 (d, C_3), 104.6 (s, C_1), 129.2 (d, 2C, Ph), 130.0 (d, 2C, Ph), 131.5 (s, Ph), 135.2 (d, Ph), 170.4 (s, $\underline{C}OOCH_2CH_3$), 189.4 (s, C_{10}), 191.8 (s, C_{12}). *Anal.* Calcd for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.82; N, 4.25. Found: C, 65.35; H, 5.84; N, 3.99.

Further elution with benzene–CH_2Cl_2 (1 : 1) and crystallization of the product from CH_2Cl_2–Et_2O gave (1*R**, 2*R**, 7*S**, 8*S**)-8-ethoxycarbonyl-1-phenyl-3-oxa-11-azatricyclo[6.3.0.^{1,8}0^{2,7}]undecan-9,10-dione (**6b**, 500 mg, 19%) colorless prisms, mp 174—175 °C. IR: 3300—3100, 1770, 1740. ^{1}H-NMR: 1.01 (3H, t, $J=7$ Hz, $COOCH_2C\underline{H}_3$), 1.60 (1H, dd, $J=4$, 12 Hz, C_6-H), 1.70 (1H, d, $J=15$ Hz, C_6-H), 1.92 (1H, m, C_5-H), 2.14 (1H, br d, $J=12$ Hz, C_5-H), 2.89 (1H, td, $J=4$, 12 Hz, C_7-H), 3.36 (1H, d, $J=12$ Hz, C_2-H), 3.59 (1H, t, $J=12$ Hz, C_4-H), 3.88 (2H, q, $J=7$ Hz, $COOC\underline{H}_2CH_3$), 4.20 (1H, dd, $J=4$, 12 Hz, C_4-H), 7.4 (3H, m, Ar-H), 7.75 (2H, m, Ar-H), 8.61 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 26.2 and 26.4 (each t, C_5 and C_6), 40.5 (d, C_7), 62.3 (t, $COO\underline{C}H_2CH_3$), 62.6 (s, C_8), 70.1 (t, C_4), 72.6 (s, C_1), 90.8 (d, C_2), 127.5 (d, 2C, Ph), 128.8 (d, 2C, Ph), 129.6 (d, Ph), 131.6 (s, Ph), 161.9 (s, C_{10}), 164.5 (s, $\underline{C}OOCH_2CH_3$), 194.5 (s, C_9). *Anal.* Calcd for $C_{18}H_{19}NO_4$: C, 65.64; H, 5.82; N, 4.25. Found: C, 65.40; H, 5.78; N, 4.03.

Crystallographic Measurement The crystal data were collected on a Rigaku Denki computer-controlled four-circle diffractometer using Cu K_α radiation. The intensities of all the reflections with 2θ values up to 140° of (*hkl*) and ($\bar{h}kl$) were measured by the ω-2θ scanning technique at a scan rate of 8° per min. The backgrounds were measured at both ends of the scan range for 5.0 s. Three standard reflections were measured every 50 min, and showed no significant variation with time. The intensity data were corrected for background count and for the usual Lorentz and polarization effects. In total, 3507 (for **5b**) and 1833 (for **6b**) independent non-zero reflections were measured.

Crystal Data: **5b**: $C_{19}H_{19}NO_4$, $M_r=325.35$. Monoclinic: $a=17.273(8)$, $b=14.424(4)$, $c=13.471(2)$ Å. $\beta=97.11(1)$. $V=3330.1$ Å^3, $D_c=1.298$ g/cm^3, $z=4$. Space group, $P2_{1/n}$; crystal size, 0.4×0.4×0.3 mm.

6b: $C_{18}H_{19}NO_5$, $M_r=329.34$. Monoclinic, $a=17.922(8)$, $b=11.821(4)$, $c=9.795(2)$ Å. $\beta=107.67(1)$. $V=1646.3$ Å^3, $D_c=1.329$ g/cm^3, $z=4$. Space group, $P2_{1/2}$: crystal size, 0.3×0.3×0.2 mm.

Structure Analysis and Refinement The structure was solved by the direct method using MULTAN[8] and refined by the block-diagonal least-squares procedure with anisotropic factors, using 3507 (for **5b**) and 1833 (for **6b**) reflections. Inclusion of hydrogen atoms with isotropic temperature factors gave the final *R*-values of 6.16% for **5b** and 7.89% for **6b**. The atomic parameters, bond lengths, and bond angles are given in Tables II—VII, respectively.

References and Notes

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