

# Dioxopyrrolines. XLVI.<sup>1)</sup> [2+2] Photocycloaddition of 4-Ethoxycarbonyl-5-phenyl-1H-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-1H-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; 1H-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-1H-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.<sup>2)</sup> 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*).<sup>3)</sup> The results could be explained by the stereoselection rule.<sup>3)</sup>

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.<sup>1,4)</sup> Dihydrofuran gave the dihydropyridone **7a** and the difurano derivative **8a**.<sup>5)</sup> 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 <sup>1</sup>H-nuclear magnetic resonance (<sup>1</sup>H-NMR) spectrum to that of **4a** except for the presence of the additional signals of one methylene group, suggesting

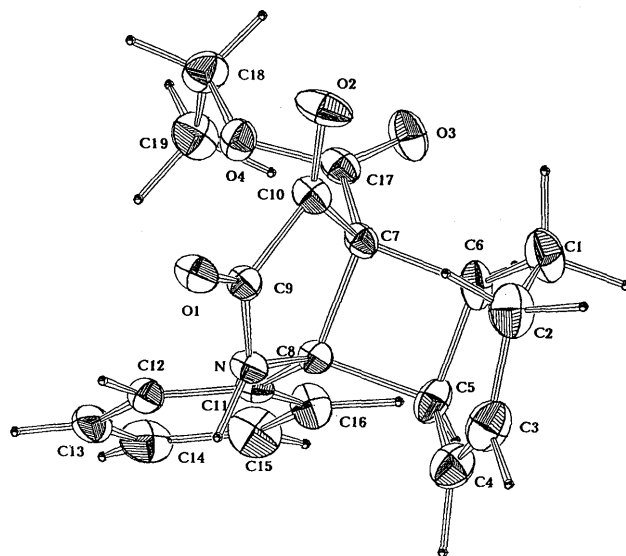
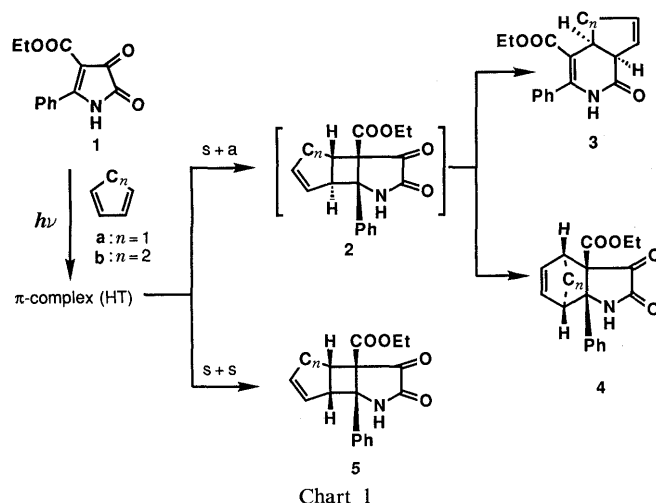


Fig. 1

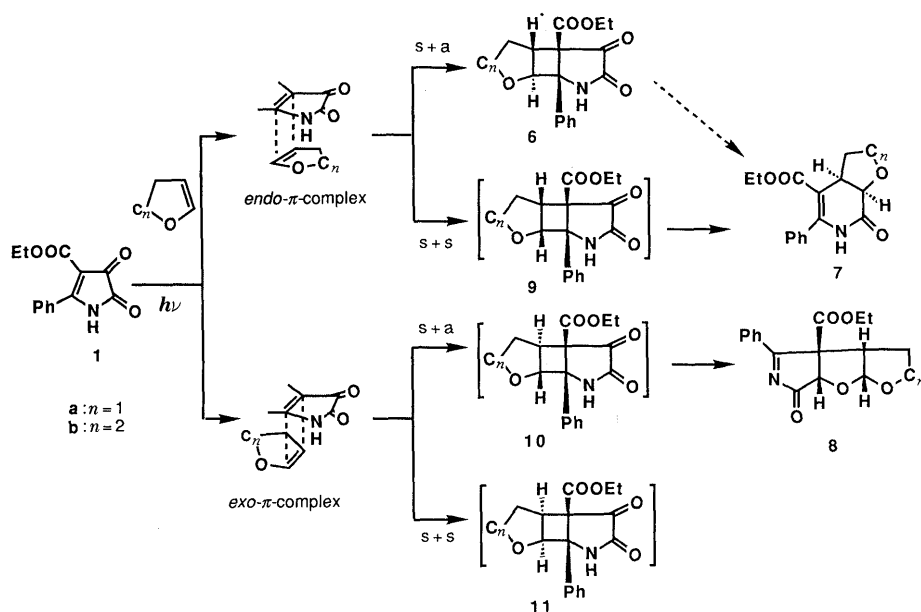


Chart 2

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

| Cycloolefins    | Stereochemical pathways % (products) <sup>a)</sup> |                                           |                                            |                 |
|-----------------|----------------------------------------------------|-------------------------------------------|--------------------------------------------|-----------------|
|                 | <i>endo</i> - $\pi$ -Pathways                      |                                           | <i>exo</i> - $\pi$ -Pathways <sup>b)</sup> |                 |
|                 | [s+s]                                              | [s+a]                                     | [s+s]                                      | [s+a]           |
| Cyclopentadiene | 10 ( <b>5a</b> )                                   | 41 { 24 ( <b>3a</b> )<br>17 ( <b>4a</b> ) | —                                          | —               |
| Cyclohexadiene  | 28 ( <b>5b</b> )                                   | 3 { 1 ( <b>3b</b> )<br>2 ( <b>4b</b> )    | —                                          | —               |
| Dihydrofuran    | 24 ( <b>7a</b> ) <sup>c)</sup>                     | —                                         | —                                          | 9 ( <b>8a</b> ) |
| Dihydropyran    | —                                                  | 19 ( <b>6b</b> )                          | —                                          | 4 ( <b>8b</b> ) |

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.

UV absorption at 280 nm and two low  $^{13}\text{C}$ -NMR signals at 189.4 and 191.8]. These and other spectral features are very similar to those of the dihydrofuran adduct **8a**,<sup>5)</sup> thus proving that **8b** is a furanopyrano derivative.

The results together with those of photocycloaddition of **1** to cyclopentadiene<sup>1,4)</sup> and to dihydrofuran<sup>5)</sup> (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<sup>1)</sup> and dihydrofuran.<sup>5)</sup> Cyclohexadiene adds to **1** preferentially in an s+s manner *via* the *endo*- $\pi$ -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.<sup>6)</sup>

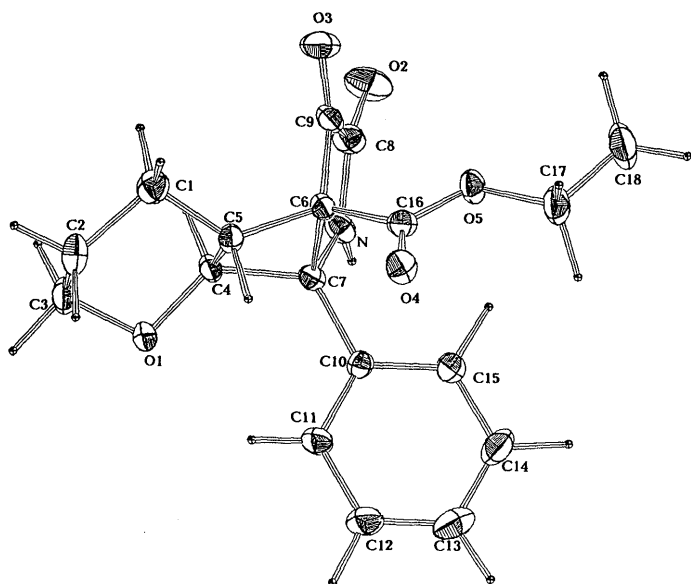


Fig. 2

that this is the hydroindole. The stereochemistry of the ethano bridge between C<sub>4</sub> and C<sub>7</sub> in **4b** was assigned by analogy with that of **4a**. The major adduct **5b** showed C-13 nuclear magnetic resonance ( $^{13}\text{C}$ -NMR) signals due to two tertiary carbons at  $\delta$  33.2 and 41.0, suggesting that it contains a cyclobutane moiety. The structure **5b** including the stereochemistry was unambiguously 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 unambiguously 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

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.<sup>3)</sup> 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 very 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  $\pi$ -complex.<sup>1)</sup> 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).<sup>3)</sup> 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.<sup>3)</sup>

If we assume that cyclohexadiene and cyclopentadiene have nearly equal contributions as electron donors, their interactions with the acceptor, dioxopyrroline, in excited  $\pi$ -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 character, 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

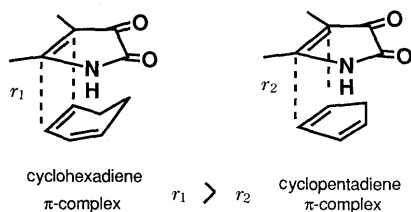


Chart 3

from an *s+s* to an *s+a*.

### 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              |

$$B_{eq} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$$

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

TABLE III. Bond Lengths ( $\text{\AA}$ ) of **5b**

| Atoms   | Distance ( $\text{\AA}$ ) |
|---------|---------------------------|
| 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  $\text{cm}^{-1}$ . UV spectra were measured in ethanol with a Hitachi 200-10 spectrophotometer and are given in  $\lambda_{\text{max}}$  (e).  $^1\text{H-NMR}$  (100 MHz) and  $^{13}\text{C-NMR}$  (25.0 MHz) spectra were taken in  $\text{CDCl}_3$  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  $\text{F}_{254}$  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 Dioxypyrroline 1 to Cyclohexadiene** A solution of **1**<sup>7)</sup> (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  $\text{SiO}_2$ . Elution with benzene- $\text{CH}_2\text{Cl}_2$  (1:1) and  $\text{CH}_2\text{Cl}_2$ , and crystallization of the product from  $\text{CH}_2\text{Cl}_2$ - $\text{Et}_2\text{O}$  gave 6-ethoxycarbonyl-2-phenyl-3-azatricyclo[5.4.0.1<sup>7,10</sup>undec-10-ene-4,5-dione (**5b**, 1.90 g, 28%) as colorless prisms, mp 178–180°C. IR: 3150–3050, 1760, 1710, 1680.  $^1\text{H-NMR}$ : 0.71 (3H, t,  $J=7$  Hz,  $\text{COOCH}_2\text{CH}_3$ ), 1.84–1.99 (4H, m,  $\text{C}_8$ -H and  $\text{C}_9$ -H), 3.6–3.8 (4H, m,  $\text{COOCH}_2\text{CH}_3$  overlapped with  $\text{C}_1$ -H and  $\text{C}_7$ ), 5.80 and 6.10 (each 1H, m,  $\text{C}_{10}$ -H and  $\text{C}_{11}$ -H), 7.3–7.6 (5H, m, ArH).  $^{13}\text{C-NMR}$ : 13.4 (q,  $\text{COOCH}_2\text{CH}_3$ ), 18.7 (t,  $\text{C}_8$ ), 21.1 (t,  $\text{C}_9$ ), 33.2 (d,  $\text{C}_7$ ), 41.0 (d,  $\text{C}_1$ ), 61.8 (t,  $\text{COOCH}_2\text{CH}_3$ ), 62.4 (s,  $\text{C}_6$ ), 64.9 (s,  $\text{C}_2$ ), 124.2 (d,  $\text{C}_{10}$  or  $\text{C}_{11}$ ), 125.6 (d, 2C, Ph), 128.5 (d, Ph), 128.7 (d, 2C, Ph), 132.3 (d,  $\text{C}_{10}$  or  $\text{C}_{11}$ ), 137.1 (s, Ph), 163.8 (s,  $\text{C}_4$ ), 166.4 (s,

$\text{COOCH}_2\text{CH}_3$ ), 195.6 (s,  $\text{C}_5$ ). Anal. Calcd for  $\text{C}_{19}\text{H}_{19}\text{NO}_4$ : 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  $\text{SiO}_2$ . Elution with hexane-benzene (3:2) and crystallization of the product from  $\text{Et}_2\text{O}$ -hexane gave (4a*R*\*, 8a*S*\*)-4-ethoxycarbonyl-3-phenyl-1,2,4a,5,6,8a-hexahydroisoquinolin-1-one (**3b**, 80 mg, 1%) as

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

| Atom | x        | y         | z         | $B_{\text{eq}}/B_{\text{iso}}$ |
|------|----------|-----------|-----------|--------------------------------|
| 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                            |

$$B_{\text{eq}} = \frac{4}{3} \sum_i \sum_j \beta_{ij} a_i a_j$$

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

TABLE VI. Bond Lengths ( $\text{\AA}$ ) of **6b**

| Atoms   | Distance ( $\text{\AA}$ ) |
|---------|---------------------------|
| 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 IV. Bond Angles ( $^\circ$ ) of **5b**

| Atoms       | Angle ( $^\circ$ ) |
|-------------|--------------------|
| 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 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). <sup>1</sup>H-NMR: 0.92 (3H, t, *J* = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 1.6–2.3 (4H, m, 2 × CH<sub>2</sub>), 3.0–3.4 (2H, m, 2 × CH), 3.96 (2H, q, *J* = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 6.00 (2H, brs, olefinic H), 7.4 (5H, brs, ArH). HRMS *m/z*: Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>: 297.1365. Found: 297.1378.

Further elution with CH<sub>2</sub>Cl<sub>2</sub> and crystallization of the product from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O gave (3aS\*, 4S\*, 7S\*, 7aS\*)-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. <sup>1</sup>H-NMR: 0.63 (3H, t, *J* = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 1.1–1.4 (4H, 2 × CH<sub>2</sub>), 3.0–3.8 (4H, m, COOCH<sub>2</sub>CH<sub>3</sub> overlapped with C<sub>4</sub> and C<sub>7</sub>-H), 6.64 (2H, m, C<sub>5</sub> and C<sub>6</sub>-H), 7.23–7.54 (5H, m, ArH). <sup>13</sup>C-NMR: 13.0 (q, COOCH<sub>2</sub>CH<sub>3</sub>), 19.5 (t, C<sub>8</sub> or C<sub>9</sub>), 21.0 (t, C<sub>8</sub> or C<sub>9</sub>), 38.3 (d, C<sub>4</sub> or C<sub>7</sub>), 41.9 (d, C<sub>4</sub> or C<sub>7</sub>), 66.6 (s, C<sub>3a</sub>), 68.0 (s, C<sub>7a</sub>), 126.0 (d, 2C, Ph), 127.8 (d, Ph), 128.2 (d, 2C, Ph), 132.3 (d, C<sub>5</sub> or C<sub>6</sub>), 133.9 (d, C<sub>5</sub> or C<sub>6</sub>), 141.4 (s, Ph), 160.2 (s, C<sub>2</sub>), 167.8 (s, COOCH<sub>2</sub>CH<sub>3</sub>), 198.7 (s, C<sub>3</sub>). Anal. Calcd for C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub> · 1/2 H<sub>2</sub>O: C, 78.25; H, 6.03; N, 4.19. Found: C, 68.77; H, 6.17; N, 3.92. HRMS *m/z*: M<sup>+</sup> Calcd for C<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>: 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<sub>2</sub>Cl<sub>2</sub>-

Et<sub>2</sub>O gave (1S\*, 3R\*, 8S\*, 9R\*)-9-ethoxycarbonyl-10-phenyl-2,4-dioxo-11-azatricyclo[7.3.0.<sup>1.9</sup>0<sup>3.8</sup>]dodec-10-en-2-one (**8b**, 105 mg, 4%) as colorless prisms, mp 173–174 °C. IR: 1750, 1720. UV: 280 (20000). <sup>1</sup>H-NMR: 1.03 (3H, t, *J* = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 1.2–1.8 (4H, m, C<sub>6</sub>-H and C<sub>7</sub>-H), 3.15 (1H, m, C<sub>8</sub>-H), 3.7 (2H, m, C<sub>5</sub>-H), 4.16 (2H, q, *J* = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 4.46 (1H, s, C<sub>1</sub>-H), 5.50 (1H, d, *J* = 3.4 Hz, C<sub>3</sub>-H), 7.5 (3H, m, Ar-H), 8.0 (2H, m, Ar-H). <sup>13</sup>C-NMR: 13.7 (q, COOCH<sub>2</sub>CH<sub>3</sub>), 21.1 and 22.1 (each t, C<sub>6</sub> and C<sub>7</sub>), 39.4 (d, C<sub>8</sub>), 62.0 (t, C<sub>5</sub>), 66.9 (s, C<sub>9</sub>), 67.7 (t, COOCH<sub>2</sub>CH<sub>3</sub>), 81.1 (d, C<sub>3</sub>), 104.6 (s, C<sub>1</sub>), 129.2 (d, 2C, Ph), 130.0 (d, 2C, Ph), 131.5 (s, Ph), 135.2 (d, Ph), 170.4 (s, COOCH<sub>2</sub>CH<sub>3</sub>), 189.4 (s, C<sub>10</sub>), 191.8 (s, C<sub>12</sub>). Anal. Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>5</sub>: C, 65.64; H, 5.82; N, 4.25. Found: C, 65.35; H, 5.84; N, 3.99.

Further elution with benzene-CH<sub>2</sub>Cl<sub>2</sub> (1:1) and crystallization of the product from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O gave (1R\*, 2R\*, 7S\*, 8S\*)-8-ethoxycarbonyl-1-phenyl-3-oxa-11-azatricyclo[6.3.0.<sup>1.8</sup>0<sup>2.7</sup>]undecan-9,10-dione (**6b**, 500 mg, 19%) colorless prisms, mp 174–175 °C. IR: 3300–3100, 1770, 1740. <sup>1</sup>H-NMR: 1.01 (3H, t, *J* = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 1.60 (1H, dd, *J* = 4, 12 Hz, C<sub>6</sub>-H), 1.70 (1H, d, *J* = 15 Hz, C<sub>6</sub>-H), 1.92 (1H, m, C<sub>5</sub>-H), 2.14 (1H, brd, *J* = 12 Hz, C<sub>5</sub>-H), 2.89 (1H, td, *J* = 4, 12 Hz, C<sub>7</sub>-H), 3.36 (1H, d, *J* = 12 Hz, C<sub>2</sub>-H), 3.59 (1H, t, *J* = 12 Hz, C<sub>4</sub>-H), 3.88 (2H, q, *J* = 7 Hz, COOCH<sub>2</sub>CH<sub>3</sub>), 4.20 (1H, dd, *J* = 4, 12 Hz, C<sub>4</sub>-H), 7.4 (3H, m, Ar-H), 7.75 (2H, m, Ar-H), 8.61 (1H, brs, NH). <sup>13</sup>C-NMR: 13.9 (q, COOCH<sub>2</sub>CH<sub>3</sub>), 26.2 and 26.4 (each t, C<sub>5</sub> and C<sub>6</sub>), 40.5 (d, C<sub>7</sub>), 62.3 (t, COOCH<sub>2</sub>CH<sub>3</sub>), 62.6 (s, C<sub>8</sub>), 70.1 (t, C<sub>4</sub>), 72.6 (s, C<sub>1</sub>), 90.8 (d, C<sub>2</sub>), 127.5 (d, 2C, Ph), 128.8 (d, 2C, Ph), 129.6 (d, Ph), 131.6 (s, Ph), 161.9 (s, C<sub>10</sub>), 164.5 (s, COOCH<sub>2</sub>CH<sub>3</sub>), 194.5 (s, C<sub>9</sub>). Anal. Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>4</sub>: 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<sub>α</sub> radiation. The intensities of all the reflections with 2θ values up to 140° of (*hkl*) and (*h̄kl*) 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<sub>19</sub>H<sub>19</sub>NO<sub>4</sub>, *M<sub>r</sub>* = 325.35. Monoclinic: *a* = 17.273(8), *b* = 14.424(4), *c* = 13.471(2) Å. β = 97.11(1). *V* = 3330.1 Å<sup>3</sup>, *D<sub>c</sub>* = 1.298 g/cm<sup>3</sup>, *z* = 4. Space group, *P*2<sub>1</sub>/*m*; crystal size, 0.4 × 0.4 × 0.3 mm.

**6b**: C<sub>18</sub>H<sub>19</sub>NO<sub>5</sub>, *M<sub>r</sub>* = 329.34. Monoclinic, *a* = 17.922(8), *b* = 11.821(4), *c* = 9.795(2) Å. β = 107.67(1). *V* = 1646.3 Å<sup>3</sup>, *D<sub>c</sub>* = 1.329 g/cm<sup>3</sup>, *z* = 4. Space group, *P*2<sub>1</sub>/*2*; crystal size, 0.3 × 0.3 × 0.2 mm.

**Structure Analysis and Refinement** The structure was solved by the direct method using MULTAN<sup>(8)</sup> 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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