Chem. Pharm. Bull. **41**(1) 64—72 (1993)

Dioxopyrrolines. LIII.[1]
Stereochemical Pathway of [2+2] Photocycloaddition Reaction of 4-Ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione to Cyclic Enol Trimethylsilyl Ethers

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Received June 16, 1992

The photocycloaddition reaction of the dioxopyrroline 1 to cyclic trimethylsilyloxy olefins was examined. The addition of 3-trimethylsilyloxy-1*H*-indene and 4-trimethylsilyloxy-1,2-dihydronaphthalene occurred in a regio- and stereoselective manner to give the *cis-anti-cis* cyclobutanes 3 and 4, respectively. The stereochemical result supported the stereo-selection rule which states that the photocycloaddition of a very polar dioxopyrroline-olefin pair proceeds in an s+s manner *via* a favored *O-endo*-π-complex transition. On the other hand, the addition of 1-trimethylsilyloxy-cyclopentene and 1-trimethylsilyloxycyclohexene occurred less stereoselectively, proceeding predominantly in an s+a manner to give the adducts 5a, b, 6a, b, 7a, b, and 12. The results are consistent with the prediction of the stereo-selection rule obtained by assuming that these dioxopyrroline–olefin pairs are polar. The latter cases demonstrate that an increased steric hindrance around the olefin moiety affects the polarity of enone-olefin pair in the transition state.

Keywords photocycloaddition; dioxopyrroline; stereochemistry; donor-acceptor interaction; cyclobutane; X-ray analysis

The stereo-selection rule[2] for the enone-olefin photocycloaddition seems to work reliably for rationalizing the stereochemical results observed in the photocycloaddition reactions of dioxopyrroline–olefin pairs.[3] The reported examples confirm 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. The donor-acceptor interaction could be evaluated in terms of the electronic properties of the two addends. In addition, it was demonstrated that the steric factor of the addends is also important in evaluating the polarity of the transition state: that is, increase of steric interaction between donor and acceptor decreases the magnitude of the donor–acceptor interaction (the polarity of the pair), which affects the stereochemical pathway of the [2+2] photocycloaddition.[3d]

The photocycloaddition reaction of 4-ethoxycarbonyl-5-phenyl-2,3-dioxo-2,3-dihydro-1*H*-pyrrole (**1**, dioxopyrroline) with acyclic enol trimethylsilyl ethers proceeded in a highly regio-selective and stereoselective manner to give the corresponding cyclobutane **2** with *O-endo* stereochemistry. This stereochemical result is consistent with the prediction (2s+2s) of the stereo-selection rule obtained by assuming that the dioxopyrroline–olefin pair is very polar, since the enol silyl ether is electron rich, and the addition proceeds *via* the *O-endo*-π-complex as a favored transition state, although the experimental evidence for this assumption is lacking. In this paper we treat the photocycloaddition reaction of the dioxopyrroline to cyclic olefins with a trimethylsilyloxy group, which is expected to provide the experimental evidence revealing the stereochemical pathway of the dioxopyrroline-very polar olefin pair as well as the steric effect of the olefinic component.

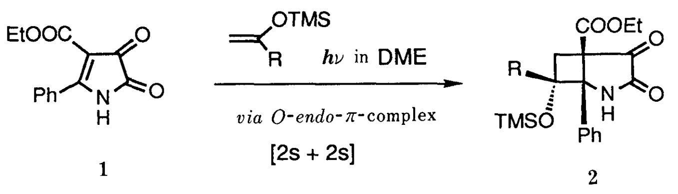

Chart 1

Results and Discussion

Irradiation of a solution of **1** and 3-trimethylsilyloxy-1*H*-indene in dimethoxyethane (DME) with a high-pressure mercury lamp gave the cyclobutane **3** as a single adduct in 49% yield. The structure of the photoadduct, except for the stereochemistry of the ring juncture, was deduced from their spectral similarity to the cyclobutanes prepared by the photocycloaddition of **1** to olefins.[3a] The structure and stereochemistry of **3** were unambiguously established by an X-ray crystallographic analysis as the cyclobutane

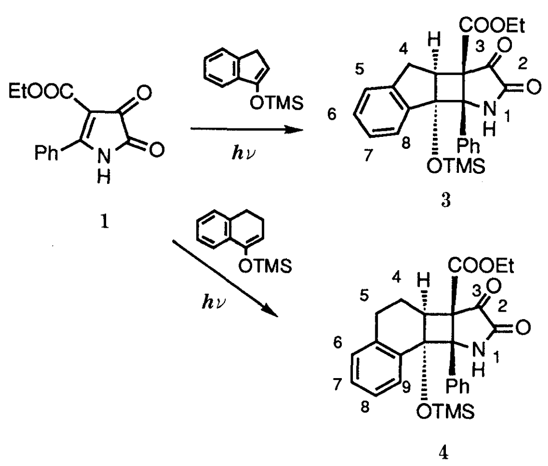

Chart 2

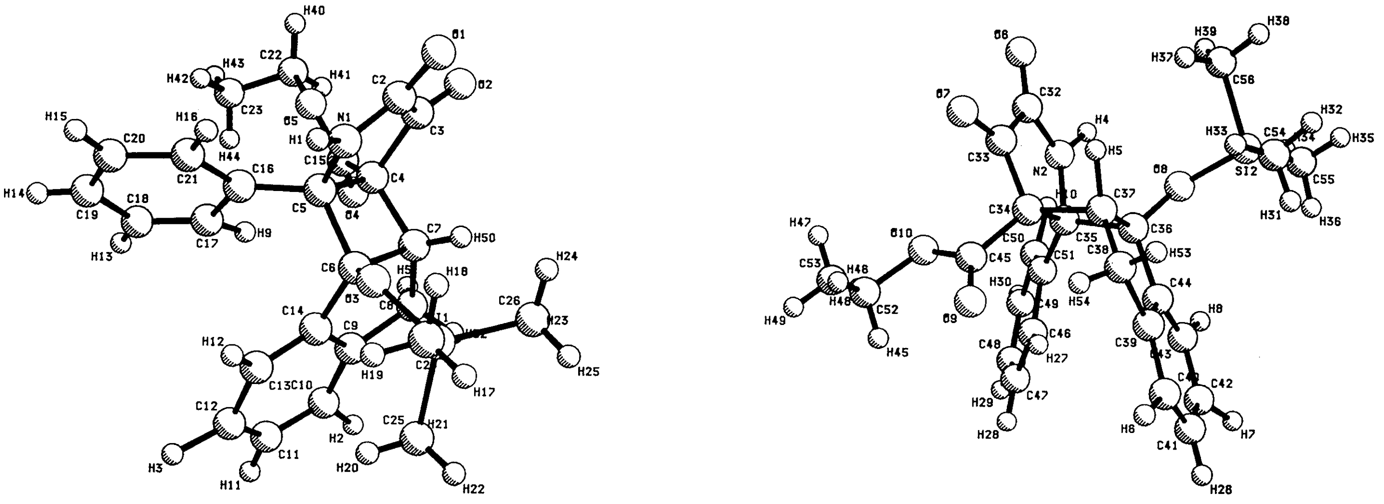

Fig. 1. Cyclobutane **3**

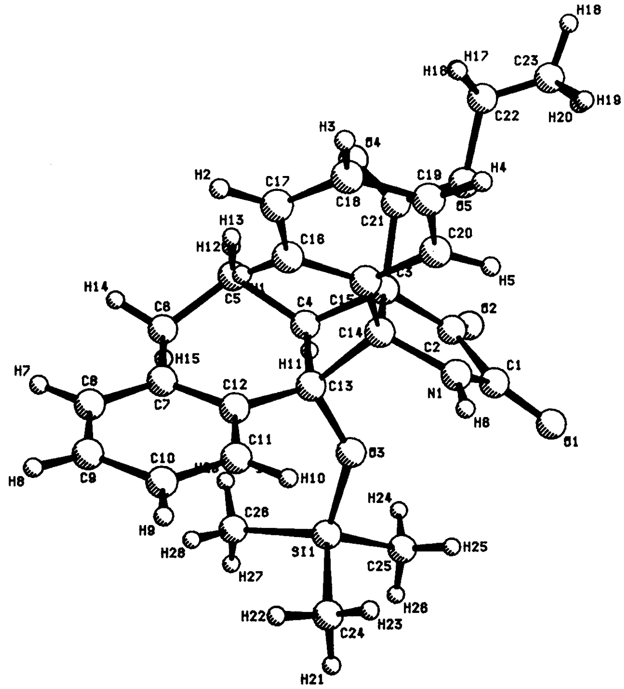

Fig. 2. Cyclobutane **4**

with *cis-anti-cis* configuration (Fig. 1).

4-Trimethylsilyloxy-1,2-dihydronaphthalene, on similar irradiation, gave the cyclobutane **4** as a single adduct in 23% yield. In contrast, 3-trimethylsilyloxy-1,2-dihydronaphthalene did not give any adduct on irradiation. In the latter case, apparent increase of the steric hindrance around the olefin may block the addition. The structure and stereochemistry of **4** were also unambiguously determined by an X-ray analysis as the cyclobutane with *cis-anti-cis* configuration (Fig. 2).

The results clearly demonstrated that the photocycloaddition of **1** to 3-trimethylsilyloxy-1*H*-indene or 4-trimethylsilyloxy-1,2-dihydronaphthalene proceeded stereoselectively in an s+s manner *via* the *O-endo-π*-complex of head to tail orientation. This stereochemical result is consistent with the prediction (s+s) of the stereoselection rule obtained by assuming that these pairs are very polar for a favored transition state. This assumption that the *O-endo-π*-complex should be most favored among stereochemically different complexes, can be rationalized since this orientation gains the maximum donor–acceptor interaction by accessing the electron-poor dioxopyrroline ring and the electron-rich enol ether moiety.

Next, we carried out photocycloaddition reactions of enol trimethylsilyl ethers of cyclopentanone and cyclohexanone. Irradiation of a solution of **1** and 1-trimethylsilyloxy-1-cyclopentene in DME for 1 h gave four adducts, **5a** (4%), **6a** (12%), **7a** (5%), and **8a** (4%). No cyclobutane derivative was isolated in this photocycloaddition.

The adduct **5a** has the molecular formula $C_{21}H_{27}NO_5Si$, indicating that the product is a 1 : 1 adduct of the addends. However, the spectral data are not consistent with the expected cyclobutane structure. The adduct exhibited a strong ultraviolet (UV) absorption band (280 nm, ε 20000) and the infrared (IR) spectra showed no signals due to an NH group. In addition to these data, the signal due to a methine proton (s, δ 5.01) in the ^{1}H-nuclear magnetic resonance (^{1}H-NMR) spectrum and the methine sp^3 carbon signal in the ^{13}C-NMR spectrum (δ 86.0) were not consistent with the cyclobutane structure. Instead, the spectral features of this adduct were compatible with the spectral data reported for the 2,4-dioxa-10-azatricyclo-[6.3.0.0^{3,7}]undecane **9**, which was generated by the photocycloaddition of **1** to dihydrofuran. The *cis-syn-cis*-stereochemistry of **9** has been unambiguously determined by an X-ray crystallographic analysis.[3b)] Thus, the adduct **5a** was assigned as a 2-oxa-5-azatricyclo[6.3.0.0^{3,7}]undecane derivative.

The major adduct **6a** has the molecular formula $C_{21}H_{29}NO_6Si$ which corresponds to a 1 : 1 adduct of addends plus H_2O. The ^{1}H- and ^{13}C-NMR spectral data were very similar to those of **5a** except for the signals attributable to the acylimino moiety, thus indicating that the adduct **6a** was a hydrate of **5**. In fact, the hydrate **6a** on heating at 200 °C under reduced pressure underwent dehydration to yield **5a**. Similarly, **5a** readily added methanol at room temperature with retention of the trimethylsilyloxy group to give the methanol adduct **10**, which was identical with the compound obtained by recrystallization of **6a** from methanol. Treatment of **5a** with acidic water caused hydration with concomitant ring

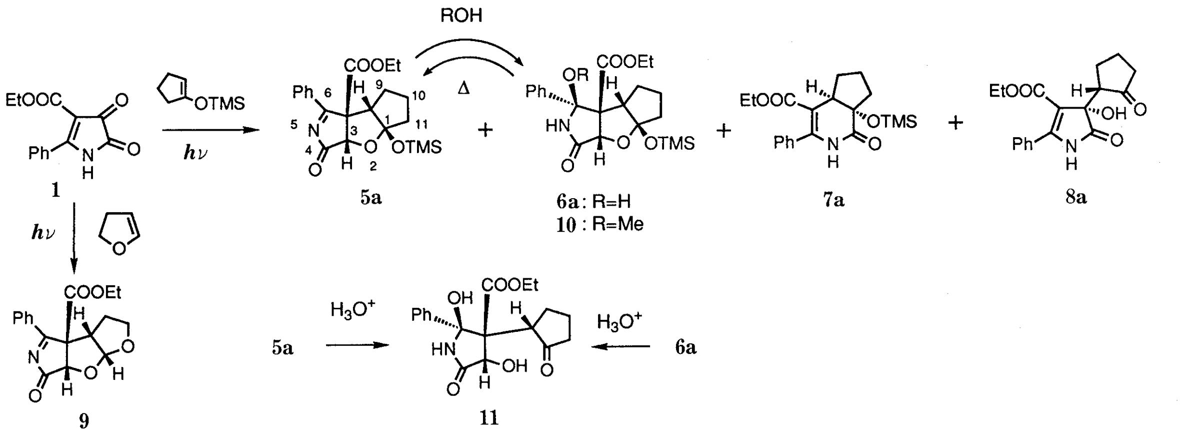

Chart 3

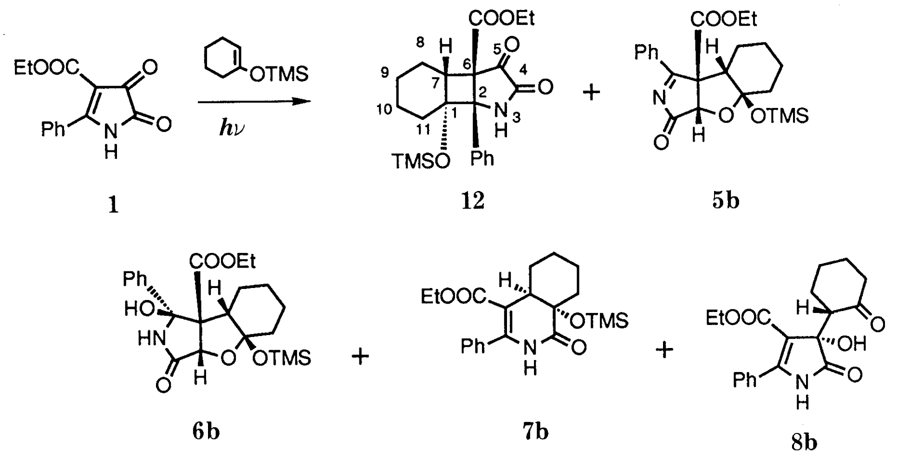

Chart 4

opening by desilylation, to give the keto-hydrate **11**, which was identical with the product derived from **6a** with a similar acidic treatment.

The observed highly stereoselective addition of water or methanol to the acylimino moiety can be reasonably explained from the assigned stereochemistry of **5a** (*cis-syn-cis*), since convex face addition of ROH to **5a** leads to the adduct **6a** with the RO group stereochemistry shown. If **5a** had different stereochemistry, such as *cis-anti-cis*, the addition of ROH would not be expected to occur stereoselectively.

The structure of **7a** was readily deduced from the spectral data. This compound has a molecular formula corresponding to a 1 : 1 adduct minus CO. The presence of the dihydropyridone moiety was revealed by the UV (285 nm) and IR spectra (1640 cm^{-1}). These were compatible with the reported data for the dihydropyridones.[3c)]

The adduct **8a** has a molecular formula corresponding to a 1 : 1 adduct minus the (TMS) group and exhibited a fairly strong UV absorption band at 309 nm (ε 6100). The IR (3200 cm^{-1}) and ^{1}H-NMR (δ 5.64, disappeared on addition of D_2O) spectra indicated the presence of an OH group. In addition to these data, the ^{1}H-NMR and ^{13}C-NMR data clearly indicated the presence of a cyclopentanone moiety. The structure **8a**, corresponding to an aldol-type condensation product to the 3-keto group of the dioxopyrroline, was obtained for the spectral similarity of the trimethylsilyloxycyclohexene adduct **8b** (see below), whose structure was established by an X-ray analysis (Fig. 4).

Similar irradiation of **1** and 1-trimethylsilyloxy-1-cyclohexene afforded five adducts, the cyclobutane **12** (6%), the acylimino derivative **5b** (4%), the hydrate derivative **6b** (3%), the dihydropyridone **7b** (1%), and the aldol-type adduct **8b** (1%).

The structure of **12** was established as the cyclobutane with *cis-syn-trans* stereochemistry by an X-ray analysis (Fig. 3) and the structure of **8b** was also determined by an X-ray analysis (Fig. 4). The structural assignment of the other adducts **5b**, **6b**, and **7b** was achieved by spectral comparison with the corresponding adducts obtained from the trimethylsilyloxycyclopentene.

The formation of **5** and **7** can be rationalized as discussed in connection with the photocycloaddition of **1** to dihydrofuran or dihydropyran.[3b,d)] The products **5** should be produced through the cyclobutane of *cis-anti-trans* configuration **13**, which was formed *via* the *O-endo*-π-complex in an s+a manner. This highly strained intermediate would decompose into **15** *via* the lactim form **14**. The resulting zwitter-ion **15** cyclizes, with rotation of the C_6–C_7 bond, followed by ketonization to give the thermodynamically more stable *cis*-fused furano derivative **5**. This mechanism explains well the stereochemistry at the four chiral centers newly formed in this reaction. On the other hand, **7** may be produced through the cyclobutane of *cis-syn-cis* configuration **16** formed *via* the *O-exo-π* complex in an s+s manner. This intermediate has favorable stereochemistry for 1,3-rearrangement through a lactim form **17**. Subsequent cheletropic loss of CO from **18** gives the dihydropyridones (**7**).

The stereochemical pathway of the photocycloaddition reactions can be summarized as shown in Table I. In the case of the trimethylsilyloxycyclopentene, the product distribution appears to be consistent with the stereoselection rule if this pair is polar, which predicts that a [2s+2a] addition and a [2s+2s] addition are preferred in the favored transition (the *O-endo-π*-complex) and in the less favored one (the *O-exo-π*-complex), respectively. The decreased polarity of this pair, when compared to the dioxopyrroline–trimethylsilyloxyindene pair (very polar pair), may be attributable to the increased steric effect due to the more puckered olefin geometry. A similar steric effect affecting the polarity of dioxopyrroline–olefin pairs and, therefore, the stereochemical pathway of their photocycloadditions was previously observed.[3c,d)]

In the case of the trimethylsilyloxycyclohexene, the cyclobutane of *cis-syn-trans* configuration **12** was isolated. The stereochemistry clearly shows that this adduct is formed in an s+a manner through the *O-exo-π*-complex. It is reasonable to consider that the product **5b**, like **5a**, is formed in an s+a manner *via* the *O-endo-π*-complex as described in the case of the trimethylsilyloxycyclopentene.

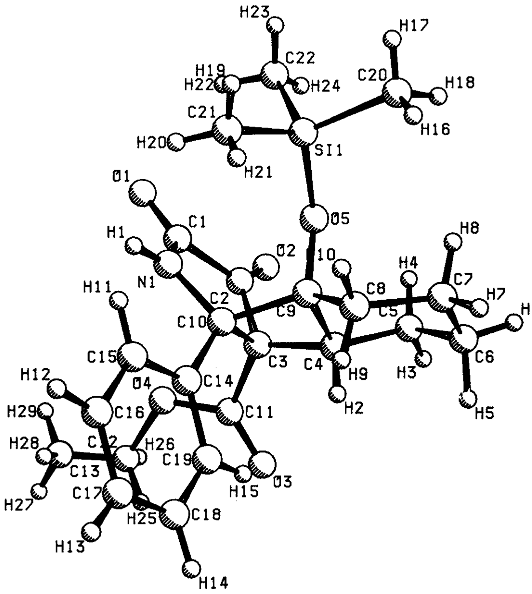

Fig. 3. Cyclobutane **12**

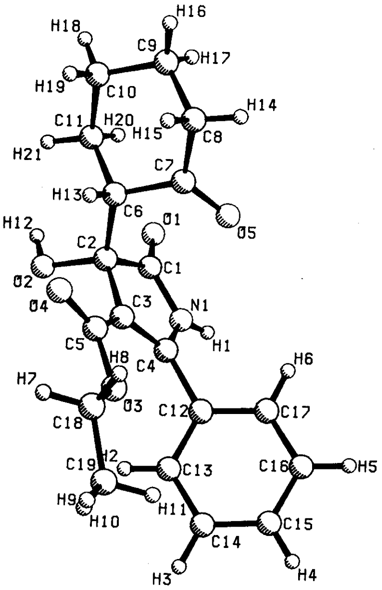

Fig. 4. Paterio–Büchi Product **8b**

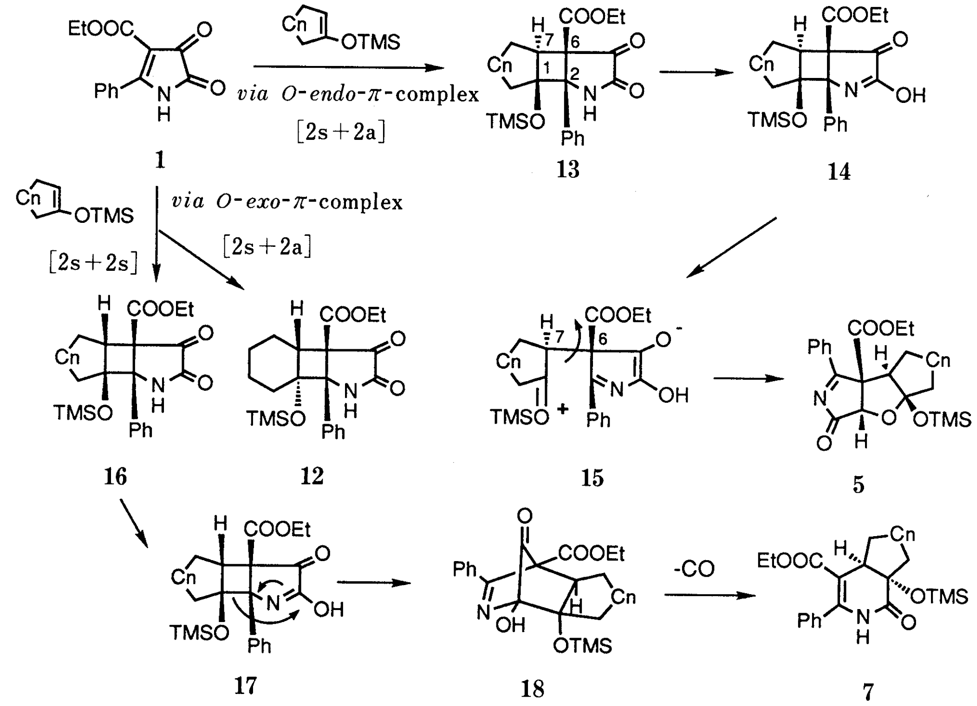

Chart 5

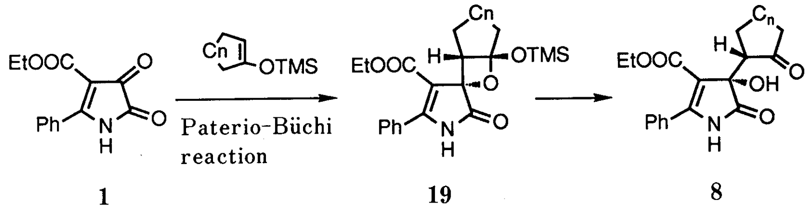

Chart 6

Table I. The Stereochemical Pathways of the Photocycloaddition Reactiqn of **1** to Trimethylsilyloxy (OTMS) Cyclic Olefins

OTMS cyclic olefins	Yields (%) of products				
	via O-endo-π- complex		*via O-exo-π-* complex		Paterio–Büchi
	s+s	s+a	s+s	s+a	
3-OTMS-indene	49 (**3**)	—	—	—	—
4-OTMS-dihydronaphthalene	23 (**4**)	—	—	—	—
1-OTMS-cyclopentene	—	16 (**5a**+**6a**)	5 (**7a**)	—	4 (**8a**)
1-OTMS-cyclohexene	—	7 (**5b**+**6b**)	1 (**7b**)	6 (**12**)	1 (**8b**)

Table II. Crystal Data for **3**, **4**, **8b**, and **12**

Compound	**3**	**4**	**8b**	**12**
Crystal forms	Monoclinic	Monoclinic	Triclinic	Monoclinic
a (Å)	12.833 (0)	14.309 (3)	9.977 (2)	15.100 (2)
b (Å)	19.546 (0)	12.593 (2)	12.374 (2)	10.626 (3)
c (Å)	20.605 (0)	15.337 (2)	7.672 (2)	15.517 (2)
α (degree)			10594 (2)	
β (degree)	107.50 (0)	116.24 (1)	96.19 (2)	116.24 (1)
γ (degree)			68.19 (1)	
V (Å^3)	4929 (0)	2478.9 (8)	845.5 (3)	2318.6 (8)
D_c (g/cm^3)	1.21	1.242	1.349	1.190
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$
Z value	8	4	2	4
Reflection observed	5018	6208	4096	5842
Reflection used for calc.	2070	2650	1746	2442
R value	0.094	0.050	0.041	0.050

The stereochemical results appear to be inconsistent with the stereo-selection rule, since both routes give the products of a [2s+2a] addition. The product ratio of the *O-endo*-pathway/the *O-exo*-pathway is roughly one, and this indicates that the transition states should be similar with respect to their transition energy. Thus, both complexes might give a [2s+2a] adduct with the stereochemistry predicted from the polar pair.

The products **8** are, in formal sense, adducts of aldol-condensation of **1** to the silyl enol ethers. However, the formation is rationalizable in terms of the Paterio–Büchi reaction[4)] rather than the aldol condensation. The [2+2] addition between the ketone of dioxopyrroline and the olefin forms the oxetane **19** and hydrolysis of the OTMS group followed by spontaneous opening of the oxetane ring gives the product **8**. The *erythro* configuration of **8** is consistent with the assumption that the [2+2] addition occurs stereospecifically, probably in an s+s manner, as shown in the Chart 6. This Paterio–Büchi reaction is the first to be observed in the photocycloaddition of **1** to olefins.

In conclusion, the results obtained by the addition of 3-trimethylsilyloxy-1H-indene and 4-trimethylsilyloxy-1,2-dihydronaphthalene to **1** confirm that the photocycloaddition of the very polar pair proceeds in an s+s manner *via* a favored transition as predicted by the stereo-selection rule. On the other hand, the photocycloaddition reactions of 1-trimethylsilyloxy-1-cyclopentene and 1-trimethylsilyloxy-1-cyclohexene to **1** gave examples showing that the steric effect due to the bulkiness around the olefin moiety lowers the polarity of the dioxopyrroline–olefin pair as described in the previous paper.[3d)]

Experimental

Unless otherwise noted, the following procedures were adopted. All melting points are uncorrected. IR spectra were measured as Nujol mulls and are given in cm^{-1}. NMR spectra were taken on a JEOL JNM-FX 100 (^{1}H-NMR, 100 MHz; ^{13}C-NMR, 25 MHz) spectrometer in $CDCl_3$ with tetramethylsilane as an internal standard and the chemical shifts are given in δ values. The following abbreviations are used; s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, and br=broad. High-resolution mass spectra (HRMS) were determined with a JEOL JMS-D 300 spectrometer at 30 eV by using a direct inlet system. UV spectra were measured in EtOH and data are given in λ_{max} nm (ε). Preparative thin layer chromatography (PTLC) was performed with precoated silica gel plates Merck 60 F_{254} (0.5 mm thick). Column chromatography was carried out with silica gel (Wakogel C-200). 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.

Photocycloaddition of 1 to 3-Trimethylsilyloxy-1*H*-indene A solution of **1** (2 g, 8 mmol) and 3-trimethylsilyloxy-1H-indene (8.4 g, 40 mmol) in DME (300 ml) was irradiated at 0 °C for 1 h. After removal of the solvent by evaporation *in vacuo*, the residue in benzene was chromatographed over SiO_2 (Mallinckrodt, CC-7). Elution with benzene–CH_2Cl_2 (1 : 1) and crystallization of the product from CH_2Cl_2–Et_2O gave *dl*-(3aR*,3bS*,8bS*,8cS*)-3a-ethoxycarbonyl-8c-phenyl-2,3-dioxo-8b-trimethylsilyloxy-1,2,3,3a,3b,4,8b,8c-octahydro-1H-indeno[2′,1′:3,4]-cyclobuta[1,2-*b*]pyrrole (**3**, 1.8 g, 49%) as colorless prisms, mp 206—207 °C. IR: 1760, 1720. ^{1}H-NMR: 0.13 (9H, s, OTMS), 0.94 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 3.42 (1H, d, J=9 Hz, H-4), 3.70 (1H, dd, J=9, 17 Hz, H-4), 3.81—4.21 (2H, m, $COOC\underline{H}_2CH_3$), 4.69 (1H, d, J=9 Hz, H-3b), 6.77—7.61 (9H, m, ArH). ^{13}C-NMR: 1.1 (3C, q, OTMS), 13.2 (q, $COOCH_2\underline{C}H_3$), 31.1 (t, C4), 50.0 (d, C3b), 56.7 (s, C3a), 61.2 (t, $COO\underline{C}H_2CH_3$), 71.9 (s, C8c), 91.6 (s, C8b), 124.9 (d, Ar), 126.3 (d, Ar), 127.6 (d, Ar), 127.8 (d, Ar), 126.6 (2C, d, Ar), 127.3 (2c, d, Ar), 129.8 (d, Ar), 134.3 (s, Ar), 140.0, 144.2 (each s, C4a, C8a), 161.3 (s, C4), 165.7 (s, $\underline{C}OOCH_2CH_3$), 195.7 (s, C3).

Photocycloaddition of 1 to 4-Trimethylsilyloxy-1,2-dihydronaphthalene A solution of **1** (2 g, 8 mmol) and 4-trimethylsilyloxy-1,2-dihydronaphthalene (8.9 g, 40 mmol) in DME (300 ml) was irradiated at 0 °C for 1 h. After removal of the solvent by evaporation *in vacuo*, the residue in benzene was chromatographed over SiO_2(Mallinckrodt, CC-7). Elution with benzene–CH_2Cl_2 (1 : 1) and crystallization of the product from CH_2Cl_2–Et_2O gave *dl*-(3aR*,3bS*,9bS*,9cS*)-3a-ethoxycarbonyl-9c-phenyl-2,3-dioxo-9b-trimethylsilyloxy-1,2,3,3a,3b,4,5,9b,9c-octahydro-1H-naphtho[2′,1′:3,4]cyclobuta[1,2-*b*]pyrrole (**4**, 880 mg, 23%) as colorless prisms, mp 241—242 °C. IR: 1770, 1740. ^{1}H-NMR: 0.15 (9H, s, OTMS), 1.12 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.79—3.23 (5H, m, H-3b, 4, 5), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 7.12—7.58 (9H, m, ArH). ^{13}C-NMR: 1.3 (3C, q, OTMS), 13.4 (q, $COOCH_2\underline{C}H_3$), 25.4 (t, C4 or C5), 27.9 (t, C4 or C5), 50.0 (d, C3b), 60.1 (s, C3a), 61.3 (t,

TABLE III. Positional Parameters and B_{eq} for the Cyclobutane **3**

Atom	x	y	z	B_{eq}
Si(1)	0.1240 (5)	0.1753 (3)	0.9204 (3)	7.6 (3)
Si(2)	0.3451 (5)	0.0707 (4)	0.5661 (3)	8.7 (4)
O(1)	0.144 (1)	0.0562 (6)	0.7026 (7)	6.9 (7)
O(2)	−0.0925 (9)	0.0549 (6)	0.6509 (6)	5.6 (6)
O(3)	0.1049 (8)	0.2041 (5)	0.8418 (6)	4.2 (5)
O(4)	−0.264 (1)	0.2051 (7)	0.6355 (6)	7.3 (8)
O(5)	−0.142 (1)	0.1963 (7)	0.5824 (7)	7.3 (8)
O(6)	0.3403 (9)	0.1832 (6)	0.7833 (7)	6.1 (6)
O(7)	0.5750 (8)	0.1903 (6)	0.8291 (6)	5.5 (6)
O(8)	0.3794 (8)	0.0379 (6)	0.6397 (5)	5.1 (6)
O(9)	0.753 (1)	0.0392 (6)	0.8427 (7)	7.3 (7)
O(10)	0.626 (1)	0.0479 (7)	0.8989 (7)	5.5 (6)
N(1)	0.113 (1)	0.1699 (7)	0.7228 (7)	4.7 (7)
N(2)	0.372 (1)	0.0719 (7)	0.7615 (6)	3.5 (6)
C(2)	0.085 (1)	0.108 (1)	0.701 (1)	5 (1)
C(3)	−0.040 (1)	0.103 (1)	0.6757 (8)	4.0 (9)
C(4)	−0.080 (1)	0.1719 (8)	0.696 (1)	4.0 (8)
C(5)	0.025 (1)	0.2155 (8)	0.7203 (8)	3.6 (8)
C(6)	0.009 (1)	0.2196 (9)	0.7928 (9)	4.3 (9)
C(7)	−0.089 (1)	0.1653 (8)	0.7673 (8)	3.3 (8)
C(8)	−0.187 (1)	0.199 (1)	0.7858 (9)	5 (1)
C(9)	−0.155 (1)	0.269 (1)	0.8055 (8)	4.2 (9)
C(10)	−0.218 (1)	0.323 (1)	0.821 (1)	5 (1)
C(11)	−0.171 (2)	0.385 (1)	0.839 (1)	6 (1)
C(12)	−0.066 (2)	0.400 (1)	0.844 (1)	6 (1)
C(13)	−0.002 (1)	0.345 (1)	0.829 (1)	5 (1)
C(14)	−0.046 (1)	0.2830 (8)	0.8081 (8)	3.7 (8)
C(15)	−0.174 (2)	0.1950 (9)	0.635 (1)	4 (1)
C(16)	0.038 (1)	0.2818 (8)	0.6867 (8)	3.2 (7)
C(17)	−0.048 (1)	0.332 (1)	0.670 (1)	5 (1)
C(18)	−0.035 (2)	0.394 (1)	0.644 (1)	6 (1)
C(19)	0.063 (2)	0.4125 (9)	0.6335 (9)	5 (1)
C(20)	0.148 (2)	0.368 (1)	0.647 (1)	6 (1)
C(21)	0.135 (1)	0.304 (1)	0.6754 (8)	5 (1)
C(22)	−0.229 (2)	0.202 (1)	0.511 (1)	10.7 (7)
C(23)	−0.230 (2)	0.271 (1)	0.499 (1)	10.9 (7)
C(24)	0.269 (2)	0.176 (1)	0.957 (1)	9.1 (6)
C(25)	0.066 (2)	0.234 (1)	0.969 (1)	10.7 (7)
C(26)	0.067 (2)	0.093 (1)	0.923 (1)	9.0 (6)
C(32)	0.400 (1)	0.137 (1)	0.7826 (8)	4 (1)
C(33)	0.523 (1)	0.1401 (9)	0.8031 (9)	4.1 (9)
C(34)	0.566 (1)	0.0756 (8)	0.7863 (8)	3.0 (8)
C(35)	0.463 (1)	0.0265 (8)	0.7621 (8)	3.3 (8)
C(36)	0.477 (1)	0.0235 (7)	0.6889 (8)	2.9 (8)
C(37)	0.571 (1)	0.0781 (8)	0.709 (1)	5 (1)
C(38)	0.670 (1)	0.0508 (9)	0.693 (1)	6 (1)
C(39)	0.641 (2)	−0.0274 (9)	0.6793 (8)	4.1 (9)
C(40)	0.711 (1)	−0.078 (1)	0.671 (1)	6 (1)
C(41)	0.666 (2)	−0.140 (1)	0.656 (1)	6 (1)
C(42)	0.557 (2)	−0.153 (1)	0.6496 (9)	6 (1)
C(43)	0.491 (1)	−0.103 (1)	0.6588 (9)	4.2 (9)
C(44)	0.534 (1)	−0.040 (1)	0.6738 (8)	4 (1)
C(45)	0.660 (2)	0.054 (1)	0.844 (1)	5 (1)
C(46)	0.542 (1)	−0.084 (1)	0.8150 (9)	5 (1)
C(47)	0.538 (2)	−0.146 (1)	0.847 (1)	6 (1)
C(48)	0.445 (2)	−0.163 (1)	0.860 (1)	7 (1)
C(49)	0.359 (2)	−0.122 (1)	0.845 (1)	7 (1)
C(50)	0.361 (1)	−0.056 (1)	0.815 (1)	5 (1)
C(51)	0.454 (2)	−0.0408 (9)	0.7997 (8)	4.0 (9)
C(52)	0.706 (2)	0.026 (1)	0.960 (1)	9 (1)
C(53)	0.655 (2)	0.019 (1)	1.004 (1)	10.4 (7)
C(54)	0.450 (2)	0.099 (1)	0.537 (1)	10.8 (7)
C(55)	0.257 (2)	0.028 (1)	0.515 (1)	13.7 (8)
C(56)	0.302 (2)	0.156 (1)	0.581 (1)	14.5 (8)
H(1)	0.2073	0.1857	0.7451	5.7
H(2)	−0.3097	0.3144	0.8264	6.7
H(3)	−0.0262	0.4570	0.8577	7.3
H(4)	0.2762	0.0671	0.7359	4.6
H(5)	0.5452	0.1369	0.7055	5.1
H(6)	0.8026	−0.0629	0.6872	7.3
H(7)	0.5005	−0.2030	0.6220	6.8
H(8)	0.3994	−0.1207	0.6432	5.8
H(9)	−0.1270	0.3111	0.6689	6.8
H(10)	0.2823	−0.0239	0.7979	6.4
H(11)	−0.2138	0.4198	0.8496	7.5
H(12)	0.0733	0.3534	0.8339	6.5
H(13)	−0.0947	0.4248	0.6331	7.7
H(14)	0.0713	0.4570	0.6163	5.8
H(15)	0.2146	0.3797	0.6388	7.4
H(16)	0.1954	0.2729	0.6866	6.1
H(17)	0.2869	0.1598	1.0029	7.0
H(18)	0.3009	0.1460	0.9319	7.0
H(19)	0.2957	0.2206	0.9565	7.0
H(20)	0.0988	0.2780	0.9708	7.0
H(21)	−0.0106	0.2380	0.9484	7.0
H(22)	0.0795	0.2174	1.0144	7.0
H(23)	−0.0093	0.0946	0.9019	7.0
H(24)	0.0997	0.0611	0.9006	7.0
H(25)	0.0813	0.0795	0.9696	7.0
H(26)	0.7104	−0.1765	0.6504	6.9
H(27)	0.6055	−0.0718	0.8032	5.7
H(28)	0.6001	−0.1751	0.8595	7.1
H(29)	0.4404	−0.2059	0.8809	8.9
H(30)	0.2943	−0.1366	0.8537	7.8
H(31)	0.4889	0.0611	0.5271	7.0
H(32)	0.4206	0.1253	0.4965	7.0
H(33)	0.4983	0.1270	0.5705	7.0
H(34)	0.1966	0.0206	0.5313	7.0
H(35)	0.2352	0.0490	0.4720	7.0
H(36)	0.2879	−0.0168	0.5101	7.0
H(37)	0.3582	0.1791	0.6123	7.0
H(38)	0.2810	0.1804	0.5381	7.0
H(39)	0.2391	0.1528	0.5963	7.0
H(40)	−0.2082	0.1772	0.4776	7.0
H(41)	−0.2986	0.1866	0.5126	7.0
H(42)	−0.1592	0.2859	0.5001	7.0
H(43)	−0.2804	0.2810	0.4557	7.0
H(44)	−0.2521	0.2950	0.5332	7.0
H(45)	0.7366	−0.0160	0.9523	7.0
H(46)	0.7615	0.0596	0.9744	7.0
H(47)	0.6246	0.0617	1.0115	7.0
H(48)	0.5972	−0.0134	0.9882	7.0
H(49)	0.7038	0.0032	1.0457	7.0
H(50)	−0.0706	0.1210	0.7869	3.9
H(51)	−0.2509	0.1983	0.7473	6.0
H(52)	−0.2018	0.1753	0.8224	6.0
H(53)	0.6796	0.0727	0.6543	6.5
H(54)	0.7342	0.0568	0.7308	6.5

COO$\underline{C}$H$_2$CH$_3$), 73.5 (s, C9c), 81.5 (s, C9b), 126.5 (d, Ar), 127.5 (2C, d, Ar), 127.6 (d, Ar), 127.8 (2C, d, Ar), 128.2 (2C, d, Ar), 129.6 (d, Ar), 134.1 (s, Ar), 134.5 (s, C5a or C9a), 138.2 (s, C5a or C9a), 164.5 (s, C2), 164.9 (s, $\underline{C}$OOCH$_2$CH$_3$), 195.5 (s, C2).

Photocycloaddition of 1 to 1-Trimethylsilyloxy-1-cyclopentene A solution of **1** (2 g, 8 mmol) and 1-trimethylsilyloxy-1-cyclopentene (6.4 g, 40 mmol) in DME (300 ml) was irradiated at 0 °C for 45 min. After removal of the solvent by evaporation *in vacuo*, the residue in benzene was chromatographed over SiO$_2$. The eluates with benzene, benzene–CH$_2$Cl$_2$ (1 : 1) and CH$_2$Cl$_2$ were purified by MPLC [with EtOAc–hexane (1 : 4 and 1 : 1)] to give **5a** (194 mg, 4%), **7a** (145 mg, 5%), **6a** (400 mg, 12%), and **8a** (100 mg, 4%).

dl-(1*R**,3*S**,7*S**,8*S**)-7-Ethoxycarbonyl-4-oxo-6-phenyl-1-trimethylsilyloxy-2-oxa-5-azatricyclo[6.3.0.0^{3,7}]undec-5-ene (**5a**): Pale yellow gum. IR: 1760, 1740. UV (dioxane): 280 (20000). ^{1}H-NMR: 0.17 (9H, s, OTMS), 1.07 (3H, t, J=7 Hz, COOCH$_2$C$\underline{H}_3$), 1.44—2.0 (4H, m, H-9, 10), 2.0—2.28 (2H, m, H-11), 3.36 (1H, t, J=8 Hz, H-8), 4.14 (2H, q, J=7 Hz, COOC$\underline{H}_2$CH$_3$), 5.01 (1H, s, H-3), 7.27—7.65 (3H, m, ArH), 8.01—8.05 (2H, m, ArH). ^{13}C-NMR: 0.9 (3C, q, OTMS), 13.6 (q, COOCH$_2\underline{C}$H$_3$), 24.0 (t, C9 or C10), 26.7 (t, C9 or C10), 36.9 (t, C11), 53.1 (d, C8), 62.1 (t, COO$\underline{C}$H$_2$CH$_3$), 67.9 (s, C7), 86.0 (d, C3), 124.5 (s,

TABLE IV. Positional Parameters and B_{eq} for the Cyclobutane **4**

Atom	x	y	z	B_{eq}
Si(1)	0.77518 (8)	0.34163 (8)	0.03940 (7)	3.94 (4)
O(1)	1.0909 (2)	0.3890 (2)	0.0765 (2)	4.7 (1)
O(2)	1.1220 (2)	0.3180 (2)	0.2683 (2)	6.6 (1)
O(3)	0.8682 (2)	0.4256 (2)	0.1058 (1)	3.64 (9)
O(4)	1.1365 (2)	0.5299 (4)	0.4480 (2)	12.0 (2)
O(5)	1.2108 (2)	0.5619 (3)	0.3535 (2)	6.9 (1)
N(1)	1.0242 (2)	0.5351 (2)	0.1196 (2)	3.2 (1)
C(1)	1.0682 (2)	0.4392 (3)	0.1327 (2)	3.6 (1)
C(2)	1.0858 (3)	0.4025 (3)	0.2341 (2)	4.1 (2)
C(3)	1.0460 (2)	0.4885 (3)	0.2702 (2)	3.5 (1)
C(4)	0.9407 (3)	0.4574 (3)	0.2789 (2)	3.7 (1)
C(5)	0.9108 (3)	0.5083 (4)	0.3529 (3)	4.7 (2)
C(6)	0.7923 (3)	0.5047 (4)	0.3121 (3)	5.2 (2)
C(7)	0.7397 (3)	0.5645 (3)	0.2176 (2)	4.3 (1)
C(8)	0.6471 (3)	0.6196 (4)	0.1927 (4)	5.6 (2)
C(9)	0.6015 (4)	0.6759 (4)	0.1079 (4)	6.4 (2)
C(10)	0.6456 (3)	0.6785 (4)	0.0442 (4)	5.8 (2)
C(11)	0.7374 (3)	0.6236 (3)	0.0672 (3)	4.4 (2)
C(12)	0.7842 (2)	0.5667 (3)	0.1526 (2)	3.5 (1)
C(13)	0.8825 (2)	0.5051 (2)	0.1756 (2)	3.1 (1)
C(14)	0.9886 (2)	0.5662 (3)	0.1911 (2)	3.1 (1)
C(15)	1.0041 (2)	0.6851 (3)	0.2094 (2)	3.4 (1)
C(16)	0.9469 (3)	0.7479 (3)	0.2417 (3)	4.4 (2)
C(17)	0.9661 (3)	0.8551 (3)	0.2577 (3)	5.5 (2)
C(18)	1.0427 (4)	0.9027 (4)	0.2416 (3)	5.6 (2)
C(19)	1.1031 (4)	0.8417 (4)	0.2125 (4)	6.6 (2)
C(20)	1.0841 (3)	0.7344 (3)	0.1969 (3)	5.5 (2)
C(21)	1.1344 (3)	0.5289 (4)	0.3714 (3)	5.4 (2)
C(22)	1.2987 (4)	0.6147 (7)	0.4316 (5)	13.6 (4)
C(23)	1.3822 (5)	0.6066 (7)	0.4346 (7)	16.5 (5)
C(24)	0.6992 (4)	0.3989 (3)	−0.0818 (3)	6.7 (2)
C(25)	0.8467 (3)	0.2227 (3)	0.0316 (3)	6.5 (2)
C(26)	0.6890 (3)	0.3082 (3)	0.0959 (3)	6.0 (2)
H(1)	0.894 (2)	0.718 (2)	0.252 (2)	3.7 (8)
H(2)	0.925 (3)	0.900 (3)	0.278 (3)	6 (1)
H(3)	1.058 (2)	0.974 (3)	0.250 (2)	4.4 (8)
H(4)	1.157 (3)	0.871 (3)	0.199 (3)	7 (1)
H(5)	1.127 (3)	0.692 (3)	0.176 (3)	8 (1)
H(6)	0.998 (2)	0.560 (2)	0.065 (2)	2.8 (7)
H(7)	0.616 (3)	0.618 (3)	0.238 (3)	7 (1)
H(8)	0.539 (3)	0.717 (3)	0.094 (3)	9 (1)
H(9)	0.617 (3)	0.718 (3)	−0.013 (3)	6 (1)
H(10)	0.767 (2)	0.625 (2)	0.022 (2)	3.5 (7)
H(11)	0.929 (2)	0.382 (2)	0.275 (2)	3.1 (7)
H(12)	0.943 (2)	0.472 (3)	0.412 (2)	4.6 (8)
H(13)	0.936 (3)	0.589 (3)	0.367 (2)	6 (1)
H(14)	0.771 (3)	0.536 (3)	0.357 (2)	5.5 (9)
H(15)	0.772 (3)	0.428 (3)	0.306 (3)	6 (1)
H(16)	1.2851	0.6889	0.4406	8.0
H(17)	1.3122	0.5835	0.4989	8.0
H(18)	1.4455	0.6385	0.4828	8.0
H(19)	1.3802	0.6445	0.3709	8.0
H(20)	1.4034	0.5353	0.4229	8.0
H(21)	0.6604	0.3472	−0.1292	7.9
H(22)	0.6467	0.4501	−0.0804	7.9
H(23)	0.7408	0.4386	−0.1043	7.9
H(24)	0.8847	0.1912	0.0958	9.4
H(25)	0.8964	0.2406	0.0085	9.4
H(26)	0.8005	0.1704	−0.0094	9.4
H(27)	0.6572	0.2406	0.0743	8.8
H(28)	0.6352	0.3604	0.0799	8.8
H(29)	0.7276	0.3061	0.1655	8.8

TABLE V. Positional Parameters and B_{eq} for the Paterio–Büchi Product **8b**

Atom	x	y	z	B_{eq}
O(1)	0.1743 (2)	0.5173 (2)	0.4285 (2)	3.7 (1)
O(2)	0.1319 (2)	0.3404 (2)	0.6002 (3)	3.6 (1)
O(3)	0.5541 (2)	0.1324 (1)	0.7595 (2)	3.5 (1)
O(4)	0.3571 (2)	0.2503 (2)	0.9235 (3)	5.9 (1)
O(5)	0.4127 (2)	0.5353 (2)	0.7692 (3)	4.3 (1)
N(1)	0.3923 (2)	0.3608 (2)	0.4102 (3)	3.6 (1)
C(1)	0.2623 (3)	0.4350 (2)	0.4855 (3)	2.9 (1)
C(2)	0.2430 (3)	0.3907 (2)	0.6471 (3)	2.7 (1)
C(3)	0.3864 (2)	0.2871 (2)	0.6465 (3)	2.6 (1)
C(4)	0.4662 (3)	0.2744 (2)	0.5061 (3)	2.8 (1)
C(5)	0.4271 (3)	0.2239 (2)	0.7895 (4)	3.0 (1)
C(6)	0.2107 (3)	0.4900 (2)	0.8263 (4)	2.9 (1)
C(7)	0.3193 (3)	0.5514 (2)	0.8736 (4)	3.4 (1)
C(8)	0.2994 (4)	0.6385 (3)	1.0579 (5)	5.6 (2)
C(9)	0.1469 (4)	0.7337 (3)	1.0729 (5)	4.9 (2)
C(10)	0.0351 (3)	0.6761 (3)	1.0268 (4)	4.4 (2)
C(11)	0.0593 (3)	0.5892 (3)	0.8396 (4)	3.8 (2)
C(12)	0.6136 (3)	0.1925 (2)	0.4443 (3)	2.8 (1)
C(13)	0.6502 (3)	0.0685 (2)	0.3917 (4)	3.7 (1)
C(14)	0.7879 (3)	−0.0056 (3)	0.3341 (4)	4.5 (2)
C(15)	0.8891 (3)	0.0438 (3)	0.3276 (4)	5.0 (2)
C(16)	0.8551 (3)	0.1658 (3)	0.3799 (4)	4.8 (2)
C(17)	0.7163 (3)	0.2404 (3)	0.4352 (4)	3.9 (2)
C(18)	0.6084 (4)	0.0681 (3)	0.8992 (4)	4.8 (2)
C(19)	0.7290 (5)	−0.0448 (4)	0.8224 (6)	6.5 (2)
H(1)	0.429 (3)	0.368 (2)	0.331 (3)	3.8 (7)
H(2)	0.580 (3)	0.037 (2)	0.398 (3)	4.4 (7)
H(3)	0.813 (3)	−0.094 (2)	0.297 (4)	5.4 (7)
H(4)	0.981 (3)	−0.007 (2)	0.291 (4)	6.0 (8)
H(5)	0.929 (3)	0.199 (3)	0.379 (4)	7.3 (9)
H(6)	0.693 (3)	0.322 (2)	0.477 (3)	4.5 (7)
H(7)	0.527 (3)	0.054 (3)	0.935 (4)	7.1 (9)
H(8)	0.636 (3)	0.126 (3)	1.006 (5)	8 (1)
H(9)	0.767 (4)	−0.095 (3)	0.906 (5)	8 (1)
H(10)	0.706 (4)	−0.092 (3)	0.719 (5)	10 (1)
H(11)	0.809 (4)	−0.029 (4)	0.789 (6)	11 (1)
H(12)	0.056 (3)	0.397 (3)	0.594 (4)	6.3 (9)
H(13)	0.218 (2)	0.452 (2)	0.919 (3)	2.9 (5)
H(14)	0.372 (3)	0.672 (3)	1.068 (5)	8 (1)
H(15)	0.307 (4)	0.596 (3)	1.155 (5)	9 (1)
H(16)	0.135 (3)	0.782 (2)	1.192 (4)	5.0 (7)
H(17)	0.133 (3)	0.786 (2)	0.986 (4)	4.9 (7)
H(18)	−0.060 (3)	0.741 (2)	1.027 (3)	4.6 (7)
H(19)	0.039 (3)	0.635 (3)	1.122 (4)	6.0 (8)
H(20)	0.052 (3)	0.633 (2)	0.747 (3)	4.1 (6)
H(21)	−0.016 (3)	0.554 (2)	0.815 (3)	4.9 (7)

C1), 128.8 (2C, d, Ph), 130.4 (2C, d, Ph), 130.6 (s, Ph), 134.8 (d, Ph), 169.4 (s, $\underline{C}OOCH_2CH_3$), 190.1 (s, C6), 192.1 (s, C4). HRMS *m*/*z*: Calcd for $C_{21}H_{27}NO_5Si(M^+)$: 401.1658. Found: 401.1671.

dl-(1*R**,3*S**,6*S**,7*S**,8*S**)-7-Ethoxycarbonyl-6-hydroxy-4-oxo-6-phenyl-1-trimethylsilyloxy-2-oxa-5-azatricyclo[6.3.0.0^{3,7}]undecane (**6a**): Colorless prisms from CH_2Cl_2–Et_2O, mp 189—191 °C. IR: 3400, 3200, 1740, 1730, 1720, 1700. ^{1}H-NMR: 0.15 (9H, s, OTMS), 1.53 (3H, t, $J=7$ Hz, $COOCH_2C\underline{H}_3$), 0.67—2.05 (6H, m, H-9, 10, 11), 2.90 (1H, t, $J=8$ Hz, H-8), 4.23—4.59 (2H, m, $COOC\underline{H}_2CH_3$), 5.33 (1H, br s, OH), 5.59 (1H, s, H-3), 7.31—7.59 (3H, m, ArH), 7.71—7.99 (2H, m, ArH), 9.30 (1H, br s, NH). ^{13}C-NMR: 0.9 (3C, q, OTMS), 14.1 (q, $COOCH_2\underline{C}H_3$), 23.1 (t, C9 or C10), 25.1 (t, C9 or C10), 35.3 (t, C11), 55.7 (d, C8), 61.7 (t, $COO\underline{C}H_2CH_3$), 68.0 (s, C7), 82.1 (d, C3), 87.8 (s, C6), 120.8 (s, C1), 126.7 (2C, d, Ph), 127.9 (2C, d, Ph), 128.7 (d, Ph), 140.4 (s, Ph), 170.6 (s, $\underline{C}OOCH_2CH_3$), 175.1 (s, C4). HRMS *m*/*z*: Calcd for $C_{21}H_{27}NO_5Si(M^+-H_2O)$: 401.1658. Found: 401.1710.

dl-(4a*R**,7a*S**)-4-Ethoxycarbonyl-1-oxo-3-phenyl-7a-trimethylsilyloxy-1,4a,5,6,7,7a-hexahydro-2*H*-cyclopenta[1,2-*c*]pyridine (**7a**): Colorless prisms from hexane–Et_2O, mp 138—140 °C. IR: 1690, 1670, 1640. UV: 285 (10000). ^{1}H-NMR: 0.14 (9H, s, OTMS), 0.94 (3H, t, $J=7$ Hz, $COOCH_2C\underline{H}_3$), 1.20—1.98 (4H, m, H-5, 6), 2.04—2.72 (2H, m, H-7), 3.23 (1H, t, $J=8$ Hz, H-4a), 3.95 (2H, q, $J=7$ Hz, $COOC\underline{H}_2CH_3$), 7.1 (1H, br s, NH), 7.26—7.44 (5H, m, ArH). ^{13}C-NMR: 1.5 (3C, q, OTMS), 13.7 (q, $COOCH_2\underline{C}H_3$), 20.4 (t, C5 or C6), 29.6 (t, C5 or C6), 35.7 (t, C7), 48.2 (d, C4a), 59.9 (t, $COO\underline{C}H_2CH_3$), 80.6 (s, C7a), 109.2 (s, C4), 127.8 (2C, d, Ph), 128.3 (2C, d, Ph), 129.1 (d, Ph), 135.9 (s, Ph), 142.8 (s, C3), 167.0 (s, $\underline{C}OOCH_2CH_3$), 171.1 (s, C1). HRMS *m*/*z*: Calcd

Table VI. Positional Parameters and B_{eq} for the Cyclobutane **12**

Atom	x	y	z	B_{eq}
Si(1)	0.53708 (7)	0.4074 (1)	0.75896 (8)	4.51 (5)
O(1)	0.5738 (2)	0.3580 (2)	1.0328 (2)	4.4 (1)
O(2)	0.7648 (2)	0.2941 (3)	1.0378 (2)	5.1 (1)
O(3)	0.9238 (2)	0.5910 (4)	1.1118 (2)	7.8 (2)
O(4)	0.8019 (2)	0.5609 (3)	1.1572 (2)	6.0 (1)
O(5)	0.6467 (2)	0.4398 (2)	0.8318 (2)	3.8 (1)
N(1)	0.6080 (2)	0.5430 (3)	0.9747 (2)	3.2 (1)
C(1)	0.6262 (2)	0.4271 (3)	1.0098 (2)	3.4 (1)
C(2)	0.7285 (2)	0.3957 (4)	1.0192 (2)	3.6 (1)
C(3)	0.7735 (2)	0.5171 (3)	1.0036 (2)	3.5 (1)
C(4)	0.8008 (2)	0.5249 (4)	0.9179 (3)	4.0 (2)
C(5)	0.8467 (3)	0.4344 (5)	0.8729 (3)	5.3 (2)
C(6)	0.8461 (4)	0.5054 (5)	0.7866 (4)	6.6 (3)
C(7)	0.7494 (4)	0.5590 (5)	0.7258 (3)	6.2 (2)
C(8)	0.6944 (3)	0.6336 (4)	0.7769 (3)	4.8 (2)
C(9)	0.6968 (2)	0.5551 (3)	0.8586 (2)	3.7 (1)
C(10)	0.6840 (2)	0.6024 (3)	0.9528 (2)	3.1 (1)
C(11)	0.8442 (3)	0.5605 (4)	1.0965 (3)	4.6 (2)
C(12)	0.8559 (5)	0.6091 (7)	1.2492 (3)	9.9 (3)
C(13)	0.8025 (6)	0.649 (1)	1.2896 (6)	24 (1)
C(14)	0.6863 (3)	0.7432 (3)	0.9656 (2)	3.4 (1)
C(15)	0.6011 (3)	0.8085 (4)	0.9424 (3)	5.0 (2)
C(16)	0.5991 (4)	0.9377 (4)	0.9492 (4)	6.3 (2)
C(17)	0.6818 (5)	1.0051 (5)	0.9794 (3)	6.4 (3)
C(18)	0.7662 (4)	0.9435 (5)	1.0012 (3)	5.9 (2)
C(19)	0.7691 (3)	0.8137 (4)	0.9947 (3)	4.9 (2)
C(20)	0.5345 (5)	0.3775 (7)	0.6404 (4)	6.7 (3)
C(21)	0.4533 (4)	0.5364 (7)	0.7544 (5)	7.1 (3)
C(22)	0.5038 (5)	0.2605 (6)	0.8033 (5)	6.7 (3)
H(1)	0.554 (2)	0.577 (3)	0.964 (2)	4.0 (8)
H(2)	0.834 (2)	0.600 (3)	0.926 (2)	3.0 (7)
H(3)	0.915 (3)	0.406 (4)	0.915 (3)	7 (1)
H(4)	0.811 (2)	0.356 (3)	0.859 (2)	4.5 (9)
H(5)	0.901 (3)	0.572 (4)	0.814 (3)	8 (1)
H(6)	0.867 (2)	0.452 (3)	0.748 (2)	4.7 (9)
H(7)	0.750 (3)	0.612 (4)	0.672 (3)	8 (1)
H(8)	0.710 (3)	0.488 (4)	0.693 (3)	6 (1)
H(9)	0.726 (2)	0.711 (3)	0.804 (2)	4.1 (8)
H(10)	0.628 (2)	0.653 (3)	0.733 (2)	3.8 (8)
H(11)	0.540 (2)	0.764 (3)	0.917 (2)	4.5 (8)
H(12)	0.536 (3)	0.975 (4)	0.930 (3)	8 (1)
H(13)	0.677 (3)	1.095 (4)	0.983 (3)	7 (1)
H(14)	0.825 (3)	0.989 (4)	1.020 (3)	7 (1)
H(15)	0.828 (2)	0.771 (3)	1.009 (2)	3.4 (8)
H(16)	0.539 (3)	0.456 (5)	0.608 (3)	8 (1)
H(17)	0.479 (4)	0.337 (5)	0.609 (3)	9 (2)
H(18)	0.582 (3)	0.312 (5)	0.639 (3)	9 (1)
H(19)	0.402 (4)	0.525 (5)	0.706 (4)	9 (2)
H(20)	0.441 (4)	0.557 (6)	0.806 (4)	11 (2)
H(21)	0.464 (5)	0.609 (6)	0.733 (5)	13 (3)
H(22)	0.489 (3)	0.273 (5)	0.860 (3)	9 (2)
H(23)	0.449 (4)	0.229 (6)	0.762 (4)	12 (2)
H(24)	0.550 (4)	0.205 (5)	0.820 (4)	10 (2)
H(25)	0.8951	0.6763	1.2438	11.9
H(26)	0.8946	0.5435	1.2852	11.9
H(27)	0.8403	0.6792	1.3495	28.8
H(28)	0.7641	0.7158	1.2546	28.8
H(29)	0.7628	0.5828	1.2953	28.8

for $C_{20}H_{27}NO_4Si(M^+)$: 373.1708. Found: 373.1743.

dl-(3*R**,1′*R**)-4-Ethoxycarbonyl-3-hydroxy-2-oxo-3-2′-oxocyclopentyl-5-phenyl-2,3-dihydro-1*H*-pyrrole (**8a**): Colorless prisms from CH_2Cl_2–Et_2O, mp 138—141 °C. IR: 3200, 1760, 1740, 1690, 1670. UV: 309 (6100). ^{1}H-NMR: 1.08 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.60—2.24 (4H, m), 2.24—2.48 (2H, m), 2.71—2.88 (1H, m), 4.06 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.64 (1H, br s, OH), 7.21—7.61 (5H, m, ArH), 8.10 (1H, br s, NH). ^{13}C-NMR: 13.8 (q, $COOCH_2\underline{C}H_3$), 20.4 (t, C4′ or C5′), 24.8 (t, C4′ or C5′), 39.1 (t, C3′), 50.8 (d, C1′), 60.2 (t, $COO\underline{C}H_2CH_3$), 80.3 (s, C3), 109.2 (s, C4), 128.1 (2C, d, Ph), 128.6 (2C, d, Ph), 129.3 (s, Ph), 130.8 (d, Ph), 153.2 (s, C5), 163.2 (s, $\underline{C}OOCH_2CH_3$), 177.2 (s, C2), 220.5 (s, C2′). *Anal.* Calcd for $C_{18}H_{19}NO_5$: C, 65.64; H, 5.82; N, 4.25. Found: C, 65.39; H, 5.66; N, 4.02. HRMS *m/z*: Calcd for M^+: 329.1264. Found: 329.1286.

Pyrrolysis of 6a Compound **6a** (50 mg) was heated neat at 205 °C under reduced pressure (5 mmHg) to give **5a** as a pale yellow oil in quantitative yield.

Methanol Adduct 10 1) Compound **5a** (50 mg) in MeOH was heated under reflux for 5 min. Evaporation of MeOH gave *dl*-(1*R**,3*S**,6*S**,7*R**,8*S**)-7-ethoxycarbonyl-6-methoxy-4-oxo-6-phenyl-1-trimethylsilyloxy-2-oxa-5-azatricyclo[6.3.0.0^{3,7}]undec-5-ene (**10**) in a quantitative yield, as colorless prisms from hexane–Et_2O, mp 218—224 °C. IR (KBr): 3332, 3200, 3100, 1719. The ^{1}H- and ^{13}C-NMR spectra of **10** in $CDCl_3$ exhibited complex signals which probably correspond to a mixture of **5a**, **10**, and methanol. The material recovered from the NMR measurement was crystallized from MeOH to give pure crystals of **10**. HRMS *m/z*: Calcd for $C_{21}H_{27}NO_5Si(M^+ - MeOH)$: 401.1632. Found: 401.1634.

2) Compound **6a** (10 mg) in MeOH (0.1 ml) was heated under reflux for 1 min. Evaporation of the solvent gave **10**.

Hydrolysis of 5a with HCl Compound **5a** (50 mg) in acetone (10 ml) and 0.01% HCl (10 ml) was stirred at room temperature for 2.5 h. After removal of the solvent *in vacuo*, the residue was crystallized from acetone to give *dl*-(3*R**,4*R**,5*R**,1′*R**)-4-ethoxycarbonyl-3,5-dihydroxy-2-oxo-4-2′-oxocyclopentyl-5-phenyltetrahydropyrrole (**11**, 25 mg) as colorless prisms, mp 206—207 °C. IR: 3400, 3170, 3080, 1740, 1722, 1705. ^{1}H-NMR (dioxane-d_6): 1.31 (3H, t, J=7 Hz, $COOCH_2CH_3$), 1.70—2.0 (7H, m), 4.1—4.3 (2H, m, $COOCH_2CH_3$), 5.15 (1H, br s), 7.3—7.4 (3H, m, Ph), 7.6—7.7 (2H, m, Ph). *Anal.* Calcd for $C_{18}H_{21}NO_6$: C, 62.24; H, 6.10; N, 4.03. Found: C, 62.10, H. 6.04; N, 3.95. MS: 329 ($M^+ - H_2O$), 246 (base peak), 200 (base peak).

Hydrolysis of 6a with HCl Compound **6a** (50 mg) in acetone (10 ml) was treated with HCl as described above to give **11** (30 mg) as colorless prisms, mp 209—211 °C.

Photocycloaddition of 1 to 1-Trimethylsilyloxy-1-cyclohexene A solution of **1** (3 g, 12 mmol) and 1-trimethylsilyloxy-1-cyclohexene (10.4 g, 60 mmol) in DME (300 ml) was irradiated at 0 °C for 45 min. After removal of the solvent by evaporation *in vacuo*, the residue in benzene was chromatographed over SiO_2. The eluates with benzene, benzene–CH_2Cl_2 (1 : 1) and CH_2Cl_2 were purified by MPLC [with EtOAc–hexane (1 : 4 and 1 : 1)] and PTLC [with EtOAc–hexane (1 : 1)] to give **12** (320 mg, 6%), **5b** (186 mg, 4%), **6b** (120 mg, 3%), **7b** (40 mg, 1%), and **8b** (50 mg, 1%).

dl-(1*R**,2*R**,6*R**,7*R**)-6-Ethoxycarbonyl-4,5-dioxo-2-phenyl-1-trimethylsilyloxy-3-azatricyclo[5.4.0.0^{2,6}]undecane (**12**): Colorless prisms from CH_2Cl_2–Et_2O, mp 198—199 °C. IR: 3200, 1780, 1720. ^{1}H-NMR: 0.19 (9H, s, OTMS), 0.94 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.22—1.70 (6H, m, H-8, 9, 10), 1.70—1.83 (2H, m, H-11), 2.80 (1H, t, J=8 Hz, H-7), 4.02 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 7.42 (5H, br s, ArH). ^{13}C-NMR: 2.1 (3C, q, OTMS), 13.7 (q, $COOCH_2\underline{C}H_3$), 19.7 (t, C9 or C10), 21.7 (t, C9 or C10), 25.2 (t, C8 or C11), 32.0 (t, C8 or C10), 47.6 (d, C7), 61.8 (t, $COO\underline{C}H_2CH_3$), 64.5 (s, C6), 74.3 (s, C2), 84.9 (s, C1), 125.1 (2C, d, Ph), 128.3 (d, Ph), 129.2 (2C, d, Ph), 133.5 (s, Ph), 165.3 (s, C4), 166.9 (s, $\underline{C}OOCH_2CH_3$), 191.7 (s, C5). HRMS *m/z*: Calcd for $C_{22}H_{29}NO_5Si(M^+)$: 415.1815. Found: 415.1852.

dl-(1*R**,3*R**,7*S**,8*R**)-7-Ethoxycarbonyl-4-oxo-6-phenyl-1-trimethylsilyloxy-2-oxa-5-azatricyclo[6.4.0.0^{3,7}]dodec-5-ene (**5b**): Pale yellow gum. IR: 1740. UV (dioxane): 281 (13000). ^{1}H-NMR: 0.17 (9H, s, OTMS), 1.06 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.18—1.92 (6H, m, H-9, 10, 11), 2.14—2.38 (1H, m, H-12), 2.48—2.76 (1H, m, H-12), 3.39 (1H, dd, J=6, 10 Hz, H-8), 4.10 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.15 (1H, s, H-3), 7.28—7.65 (3H, m, ArH), 8.13—8.22 (2H, m, ArH). ^{13}C-NMR: 1.5 (3C, q, OTMS), 13.6 (q, $COOCH_2\underline{C}H_3$), 22.5, 23.5, 26.3 (each t, C9, C10, or C11), 35.2 (t, C12), 48.6 (d, C8), 62.0 (t, $COO\underline{C}H_2CH_3$), 72.0 (s, C7), 83.3 (d, C3), 128.8 (2C, d, Ph), 130.8 (2C, d, Ph), 131.3 (s, Ph), 134.8 (d, Ph), 169.6 (s, $\underline{C}OOCH_2CH_3$), 190.0 (s, C6), 192.4 (s, C4). HRMS *m/z*: Calcd for $C_{22}H_{29}NO_5Si(M^+)$: 415.1813. Found: 415.1802.

dl-(1*R**,3*S**,6*S**,7*R**,8*S**)-7-Ethoxycarbonyl-6-hydroxy-4-oxo-6-phenyl-1-trimethylsilyloxy-2-oxa-5-azatricyclo[6.4.0.0^{3,7}]dodecane (**6b**): Colorless prisms from CH_2Cl_2–Et_2O, mp 176—177.5 °C. IR: 3400, 3200, 1720, 1700. ^{1}H-NMR: 0.16 (9H, s, OTMS), 1.05 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.2—1.95 (7H, m, H-9, 10, 11, 12), 2.2—2.4 (1H, m, H-12), 3.22 (1H, dd, J=6, 13 Hz, H-8), 4.10 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.16 (1H, s, H-3), 7.3—7.6 (3H, m, ArH), 8.19 (2H, m, ArH), 9.19 (1H, br s, NH). ^{13}C-NMR: 0.9 (3C, q, OTMS), 14.0 (q, $COOCH_2\underline{C}H_3$), 22.5, 24.2, 25.0 (each t, C9, C10 or C11), 35.8 (t, C12), 50.8 (d, C8), 61.1 (t, $COO\underline{C}H_2CH_3$), 69.4 (s, C7), 80.6 (d, C3), 87.1 (s, C6), 109.6 (s, C1), 126.6 (2C, d, Ph), 127.6 (2C, d, Ph), 128.1 (d, Ph), 141.4 (s, Ph), 174.1 (s, $\underline{C}OOCH_2CH_3$), 174.8 (s, C4). HRMS *m*/*z*: Calcd for $C_{19}H_{29}NO_5(M^+-TMS)$: 343.1420. Found: 343.1446.

dl-(4a*R**,8a*R**)-4-Ethoxycarbonyl-1-oxo-3-phenyl-8a-trimethylsilyloxy-1,2,4a,5,6,7,8,8a-octahydroisoquinoline (**7b**): Colorless prisms from hexane–Et_2O, mp 203—205 °C. IR: 1680, 1640. UV: 286 (10000). ^{1}H-NMR: 0.13 (9H, s, OTMS), 0.90 (3H, t, $J=7$ Hz, $COOCH_2C\underline{H}_3$), 1.20—1.84 (6H, m, H-6, 7, 8), 1.92—2.16 (1H, m, H-5), 2.52—2.70 (1H, m, H-5), 2.90 (1H, dd, $J=4$, 11 Hz, H-4a), 3.93 (2H, q, $J=7$ Hz, $COOC\underline{H}_2CH_3$), 7.07 (1H, br s, NH), 7.27—7.51 (5H, m, ArH). HRMS *m*/*z*: M^+ Calcd for $C_{21}H_{29}NO_4Si$: 387.1864. Found: 387.1856.

dl-(3*R**,1′*R**)-4-Ethoxycarbonyl-3-hydroxy-2-oxo-3-2′-oxocyclohexyl-5-phenyl-2,3-dihydro-1*H*-pyrrole (**8b**): Colorless prisms, mp 166—168 °C from CH_2Cl_2–Et_2O. IR: 3350, 1720, 1700, 1680. UV: 236 (12000), 300 (8000). ^{1}H-NMR: 1.03 (3H, t, $J=7$ Hz, $COOCH_2C\underline{H}_3$), 1.44—2.60 (8H, m), 3.50 (1H, dd, $J=5.5$, 12 Hz, H-1′), 3.90 (1H, s, OH), 4.03 (2H, q, $J=7$ Hz, $COOC\underline{H}_2CH_3$), 7.36—7.59 (5H, m, ArH), 8.02 (1H, br s, NH). ^{13}C-NMR: 13.8 (q, $COOCH_2\underline{C}H_3$), 25.0, 27.2 27.4 (each t, C4′, C5′ or C6′), 42.5 (t, C3′), 56.2 (d, C1′), 60.0 (t, $COO\underline{C}H_2CH_3$), 77.4 (s, C3), 109.3 (s, C4), 127.9 (2C, d, Ph), 128.6 (2C, d, Ph), 130.0 (d, Ph), 130.5 (s, Ph), 153.6 (s, C5), 163.8 (s, $\underline{C}OOCH_2CH_3$), 177.7 (s, C2), 211.7 (s, C2′). *Anal.* Calcd for $C_{19}H_{21}NO_5$: C, 66.46; H, 6.16; N, 4.08. Found: C, 66.15; H, 6.06; N, 4.14. HRMS *m*/*z*: Calcd for M^+: 343.1420. Found: 343.1455.

X-Ray Crystallographic Analyses The reflection data were collected on a Rigaku AFC-5 four-circle diffractometer using graphite-monochromated MoK_α radiation in the ω–2θ scan mode at a 2θ scan speed of 4°/min for $3° < 2\theta < 55°$. Of the reflections collected, those above the $3\sigma(I)$ level were used for the calculation. The structures of **3**, **4**, **8b**, and **12** were solved by the direct method using MITHRIL[5)] and refined by the full matrix least-squares procedure with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms. Some hydrogen atoms were located at calculated positions. The crystal data for **3**, **4**, **8b**, and **12** are collected in Table II and the atomic parameters of these compounds are listed in Tables III, IV, V, and VI.

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