Dioxopyrroline. LIV.[1] Stereochemical Pathway of [2+2]Photocycloaddition Reaction of 4,5-Diethoxycarbonyl-1*H*-pyrrole-2,3-dione to Acyclic Olefins

Takehiro SANO,*[a] Hiroshi ENOMOTO,[a] Yasuko KUREBAYASHI,[a] Yoshie HORIGUCHI,[a] and Yoshisuke TSUDA[b]

Showa College of Pharmaceutical Sciences,[a] 3–3165 Higashi-tamagawa-gakuen, Machida-shi, Tokyo 194, Japan and Faculty of Pharmaceutical Sciences,[b] Kanazawa University, 13–1 Takara-machi, Kanazawa 920, Japan. Received July 31, 1992

The photocycloaddition reaction of 4,5-diethoxycarbonyl-1*H*-pyrrole-2,3-dione 4 to acyclic olefins proceeded in a regioselective manner to give two head to tail adducts, the *exo*- (5) and *endo*-isomers (6). The stereochemistry of the 7-substituents of the adducts changed depending on the electronic properties of olefins. Olefins with *O*-substituents (ethoxyethylene, acetoxyethylene) stereoselectively gave the *endo*-adducts (6d, e). Olefins with phenyl and ethyl substituents, styrene and 1-butene, gave a mixture of the *exo*- (5a, b) and *endo*-adducts (6a, b) with *exo*-preference. Butadiene gave the *exo*- (5b) and *endo*-adduct (6b) with slight excess of the latter. These stereochemical results are in good accordance with the predictions obtained by the stereo-selection rule of enone–olefin photocycloaddition.

Keywords [2+2] photocycloaddition; stereochemistry; dioxopyrroline; stereo-selection rule; enone–olefin photocycloaddition; cyclobutane

The [2+2] photocycloaddition reaction of enones to olefins has been widely utilized for construction of complex molecules.[2] However, the stereochemical aspects of the reaction still remain to be clarified. Recently, we showed that the stereochemistry in the photocycloaddition reaction of 4-ethoxycarbonyl-5-phenyl-1*H*-pyrrole-2,3-dione **1** (4-COOEt-5-Ph-dioxopyrroline) to acyclic olefins leading to cyclobutanes with head-to-tail (H-T) regiochemistry changed depending on the electronic properties of the olefins.[3] Olefins with a strong electron-donating substituent (strong electron donors) give the *endo*-adducts **3**, in which addition of the olefin had proceeded in an s+s manner, while those with a weak electron donating substituent (weak electron donors) give the *exo*-adducts **2**, in which addition of the olefin had proceeded in an s+a manner. The results could be explained by the stereo-selection rule which was proposed by us.[4] Furthermore, formation mechanisms of various photoadducts in the photocycloaddition reactions of **1** with cyclic olefins could be rationalized by assuming that the intermediary cyclobutane possesses the stereochemistry predicted from the stereo-selection rule.[1,5]

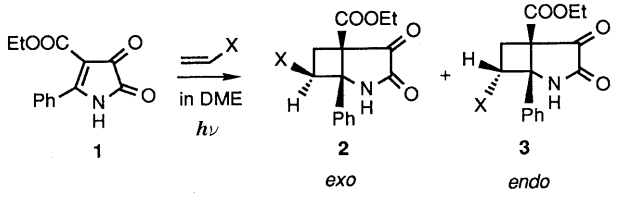
In this paper we describe the photocycloaddition reaction of 4,5-diethoxycarbonyl-1*H*-pyrrole-2,3-dione **4** (4,5-diCOOEt-dioxopyrroline) with acyclic olefins. The replacement of the phenyl group with an ethoxycarbonyl group at the 5-position of the dioxopyrroline may change the electronic properties of the double bond and, therefore, may affect the stereochemical pathway in the [2+2] photocycloaddition reaction.

Results and Discussion

Irradiation of a solution of the 4,5-diCOOEt-dioxopyrroline **4** with various electron-rich olefins (styrene, butadiene, 1-butene, ethoxyethylene, acetoxyethylene) in benzene with ≥300 nm light gave two stereoisomeric cyclobutanes **5** and **6** in moderate yields. In the case of isoprene, the [4+2] adduct **7f** was isolated as a minor product, together with the cyclobutanes **5f** and **6f**. The ratio of each product was determined by chromatographic isolation from the product mixture. Olefins carrying the electron-donating substituents shown in Table I underwent cycloaddition in a regioselective manner to give the cyclobutanes. On the other hand, the olefin possessing an electron-accepting group (methyl acrylate) did not undergo cycloaddition to **4** to any significant extent. The photocycloaddition in dimethoxyethane (DME) solution, instead of benzene solution gave the same products in lesser yields, and the stereochemical results were almost the same (Table I).

The structure and stereochemistry of the [2+2] adducts were elucidated as follows. Treatment of the styrene adduct **6a** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at room temperature caused a ring expansion reaction to give the 1,5-dihydro-2*H*-azepine-2-one **8** (25%).[6] Observation of an OH signal (3230 cm^{-1}) in the infrared (IR) spectrum and a strong absorption band (λ_{max} 317 nm) in the ultraviolet (UV) spectrum indicated the dihydroazepinone structure. In particular, the presence of the 5-methylene proton signal (δ 3.34) as a singlet in the ^{1}H-nuclear magnetic resonance (NMR) spectrum supported the structure **8**, excluding the other regioisomeric structure **8'**. These facts indicate that the adduct **6a** has the H-T-regiochemistry. The isomer **5a** under similar basic treatment did not undergo ring expansion, and under a drastic condition (heated at 100 °C) it extensively decomposed giving no characterizable product.

The following chemical transformations confirmed that the adducts **5a** and **6a** are the 7-epimers. Treatment of **5a**



a: X=Ph, b: X=vinyl, c: X=Et, d: X=OEt, e: X=OAc

Chart 1

and **6a** with triethyloxonium fluoroborate (Meerwein reagent) gave the corresponding imidate **9** and **10**, respectively. Pyrolysis of **9** at 250 °C for 5 h followed by chromatography over silica gel gave the dihydropyridone **11** (24%) and the pyridine **12** (11%). Similar pyrolysis of **10** under a more drastic condition (300 °C, 8 h) gave the same products, **11** (1%) and **12** (27%). The structures of the pyrolysates were deduced from their molecular weights and characteristic UV spectra (λ_{max} 282 nm for **11** and 283 nm for **12**). Formation of **11** and **12**, as already discussed in the similar reaction of 1-phenyl analogs,[7] can be explained in terms of the 1,3-shift of the C_1–C_7 bond to the C_3 position and cheletropic loss of CO from the resulting azanorbornene **13**, giving rise to the dihydropyridine **14**, which was converted on hydrolysis to **11** or on dehydrogenation (probably by air) to **12**. The stereochemistry of the 7-phenyl group was determined from the ^{1}H-NMR spectra (see below).

The structures of the butadiene adducts, including the stereochemistry of the 7-vinyl group, were elucidated by means of chemical transformations. Pyrolysis of **5b** caused a 1,3 shift of the C_1–C_7 bond to the vinyl carbon to give the hydroindole **15**. The adduct **6b** on pyrolysis was also converted into the same hydroindole **15**. This was identical with the adduct obtained by Diels–Alder reaction of **4** with butadiene,[8] thus, establishing the structures of **5b** and **6b** as cyclobutanes of 7-epimers.

The stereochemistry of the 7-vinyl group was deduced from the following chemical transformations. Treatment of **5b** with Meerwein reagent gave the corresponding imidate **16**, which on pyrolysis at 200 °C for 3 h followed by chromatography on silica gel gave the hydroindole **17** as a major product (29%) and the aza-Cope product **19** as a minor product (4%). Compound **17** was identical with the

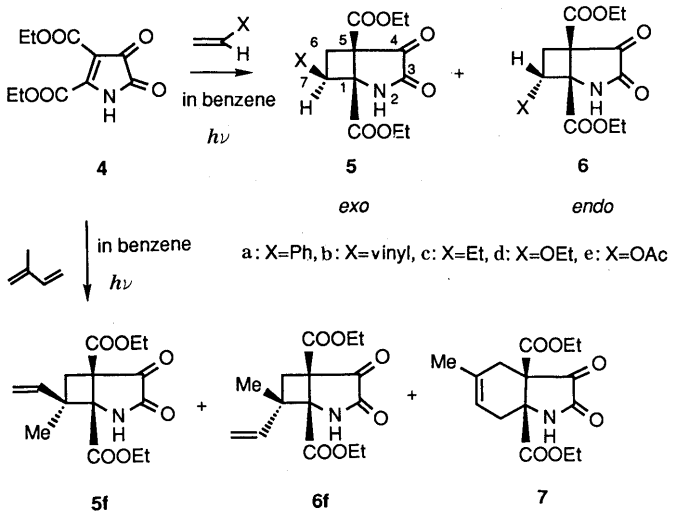
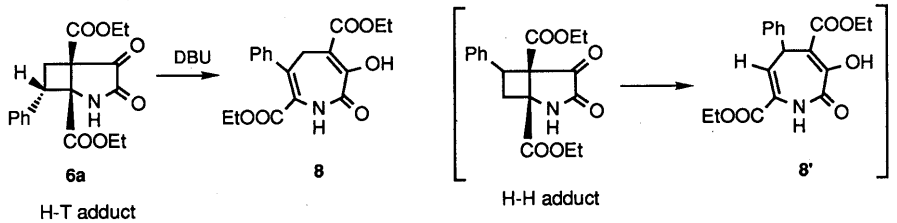


Chart 2

Table I. Photocycloaddition of 4,5-DiCOOEt-dioxopyrroline **4** with Acyclic Olefins

Olefin	Conditions[a]		Products (yield %)		
	Solvent	Time (min)	**5**	**6**	Others
a: Styrene	Benzene	45	21	12	—
	DME	45	9	4	—
b: Butadiene	Benzene	45	18	19	—
	DME	45	9	16	—
c: 1-Butene	Benzene	60	21	11	—
d: OEt-ethylene	Benzene	45	—	28	—
	DME	45	—	17	—
e: OAc-ethylene	Benzene	60	—	38	—
	DME	60	—	—[c]	
f: Isoprene	Benzene	45	26	15	4[b]
	DME	45	2	2	5[b]

a) Irradiation was done at 0 °C. *b*) The product is the hydroindole **7**. *c*) No characterizable product was isolated.



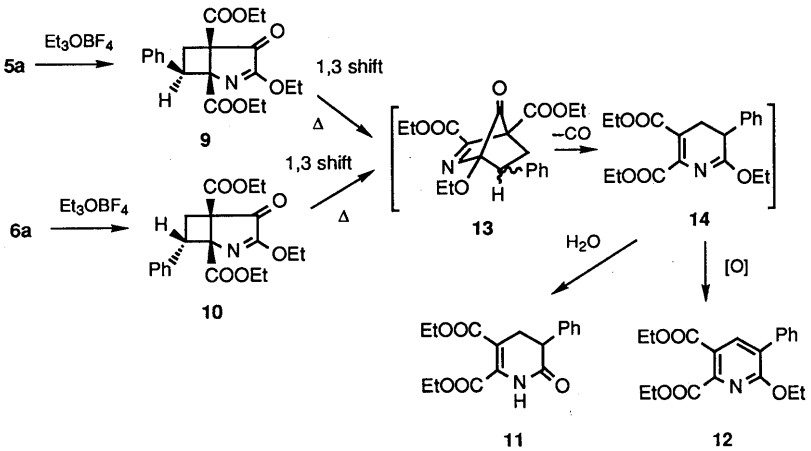


Chart 3

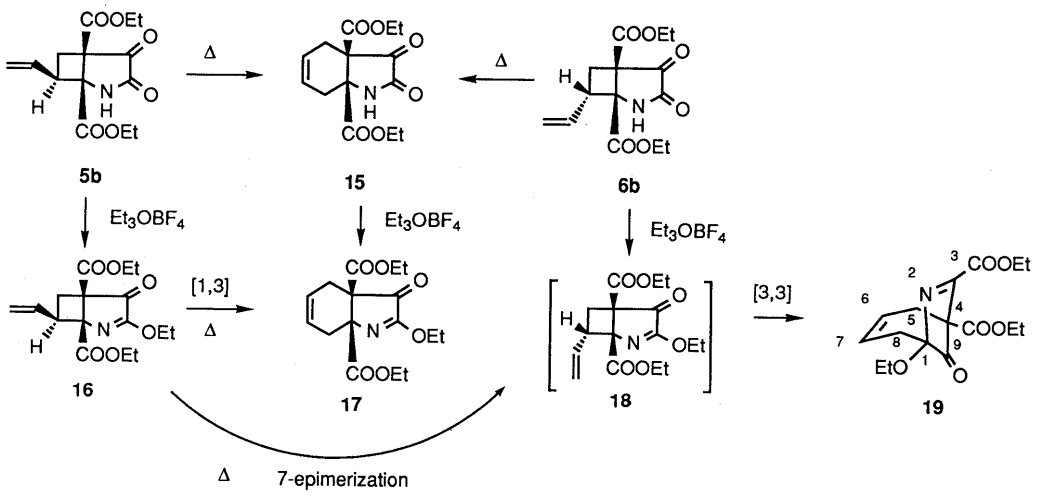


Chart 4

TABLE II. Chemical Shifts (δ_H) of 7-H in the ^{1}H-NMR Spectra of the Cyclobutanes **2**, **3**, **5**, and **6**

7-X	Cyclobutane (stereochemistry of 7-X)					
	5 (*exo*)	**6** (*endo*)	$\Delta\delta_{5-6}$	**2** (*exo*)[3]	**3** (*endo*)[3]	$\Delta\delta_{2-3}$
a: Ph	3.80	4.53	−0.73	4.17	4.85	−0.68
b: Vinyl	2.98	3.76	−0.63	3.32	4.13	−0.81
c: Et	2.35	3.08	−0.53	2.70	3.30	−0.60
d: OEt	—	4.46	—	4.12	4.75	−0.63
e: OAc	—	5.29	—	5.01	5.89	−0.88

TABLE III. Chemical Shifts (δ_C) of 7-C in the ^{13}C-NMR Spectra of the Cyclobutanes **2**, **3**, **5**, and **6**

7-X	Cyclobutane (stereochemistry of 7-X)					
	5 (*exo*)	**6** (*endo*)	$\Delta\delta_{5-6}$	**2** (*exo*)[3]	**3** (*endo*)[3]	$\Delta\delta_{2-3}$
a: Ph	52.5	43.4	9.1	54.3	43.3	11.0
b: Vinyl	50.4	42.3	8.1	52.1	41.6	10.5
c: Et	49.8	41.7	8.1	52.1	42.7	9.4
d: OEt	—	74.0	—	83.3	75.6	7.7
e: OAc	—	68.7	—	—	68.3[a]	—

a) ^{13}C-NMR of **3e**: 13.3 (q, $COOCH_2\underline{C}H_3$), 20.4 (q, $OCO\underline{C}H_3$), 30.2 (t, C6), 56.4 (s, C5), 62.1 (t, $COO\underline{C}H_2CH_3$), 66.7 (s, C1), 68.3 (d, C7), 125.8 (d, 2C, Ph), 128.7 (d, 2C, Ph), 129.0 (d, Ph), 135.0 (s, Ph), 161.7 (s, C3), 165.6 (s, $\underline{C}OOCH_2CH_3$), 170.2 (s, $O\underline{C}OCH_3$), 193.8 (s, C4).

TABLE IV. Chemical Shifts (δ_H) of 6-H in the ^{1}H-NMR Spectra of the Cyclobutanes **2**, **3**, **5**, and **6**

7-X		1-Ph-cyclobutane[3]			1-COOEt-cyclobutane		
			6-*endo*-H	*exo*-H		6-*endo*-H	*exo*-H
Ph	*exo*	**2a**	2.70	3.56	**5a**	2.59	3.43
Ph	*endo*	**3a**	2.49	3.39	**6a**	2.48	3.36
Vinyl	*exo*	**2b**	2.47	3.16	**5b**	2.40	2.98
Vinyl	*endo*	**3b**	2.19	3.16	**6b**	2.20	3.23
OEt	*exo*	**2d**	2.59	3.15	**5d**	—	—
OEt	*endo*	**3d**	2.17	3.33	**6d**	2.13	3.29
OAc	*exo*	**2e**	2.66	3.33	**5e**	—	—
OAc	*endo*	**3e**	2.31	3.46	**6e**	2.33	3.45

imidate prepared from the Diels–Alder adduct **15**. On the other hand, the cyclobutane **6b**, on imidation with Meerwein reagent, was not converted to the corresponding cyclobutane imidate **18** but exclusively provided the aza-Cope product **19**. Since this [3,3] sigmatropic rearrangement is characteristic of the intermediary 7-*endo* vinyl imidate,[9] the above result established the stereochemistry of 7-vinyl group in **6b** as *endo*. The formation of **19** from the isomer **16** at the higher temperature can be rationalized in terms of the epimerization of the vinyl group prior to the [3,3] sigmatropic rearrangement. Such a thermal epimerization of the 7-vinyl group was also observed in the 1-phenyl analog.[9] Thus, **5b** must be the 7-*exo*-isomer.

The structure and stereochemistry of 1-butene photoadducts **5c** and **6c** were established by chemical correlation with the butadiene adducts. Catalytic hydrogenation of the *exo*-isomer **5b** over 5% Pd–C gave the dihydro derivative, which was identical with the major adduct **5c**, thus proving that it is the 7-*exo*-isomer. A similar catalytic hydrogenation of the *endo*-isomer **6b** gave the minor adduct **6c**, thus proving it to be the 7-*endo*-isomer.

In a previous paper[3] we demonstrated that the *exo*-isomer **2** and *endo*-isomer **3** from the 4-COOEt-5-Ph-dioxopyrroline **1** are distinguishable by examination of their NMR spectra. In the ^{1}H-NMR spectra, the C_7-H (geminal to the substituent) of the *exo*-isomer **2** resonates at higher field than that of the *endo*-isomer **3** (Table II). The chemical shift of the 7-carbon in the ^{13}C-NMR spectra also differentiates the two isomers: that of the *exo*-isomer **2** resonates at lower field than that of the *endo*-isomer **3** (Table III). These relationships seem to hold for the butadiene and 1-butene adducts of 4,5-diCOOEt dioxopyrroline **4**; that is, the *exo*-isomers **5b** and **5c** exhibited the C_7-H signals at higher field and the 7-carbon signals at lower field than those of the corresponding *endo*-isomers **6b** and **6c**, respectively.

The major adduct **5a** from styrene gave the C_7-H signal at higher field and the 7-carbon signal at lower field than those of the minor product **6a**. Thus, the configuration of the 7-phenyl group of **5a** and **6a** was concluded to be *exo* and *endo*, respectively.

The method of differentiating the 7-epimers described above could not be applied for the ethoxyethylene adduct **6d** and the acetoxyethylene adduct **6e**, since in these cases

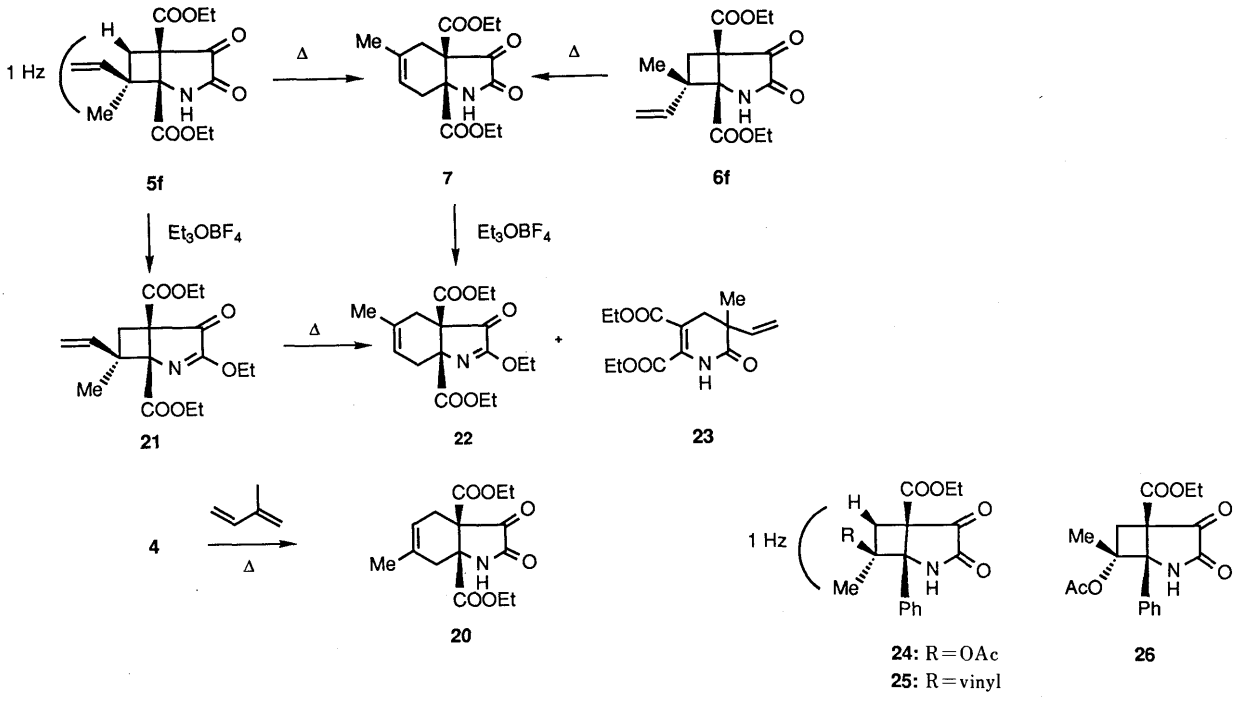


Chart 5

the 7-epimers **5d** and **5e** were not available. However, the stereochemistry of their 7-substituents was deduced to be *endo* from the following NMR spectral analyses. The ^{1}H-NMR spectral data of the cyclobutanes (Table IV) demonstrate that the signals of 6-*endo*-H and 6-*exo*-H on the cyclobutane ring appear at similar nuclear magnetic field whether the C_1-substituent is phenyl or ethoxycarbonyl, provided the 7-substituent (X) and its configuration are the same. For example, the 6-H signals of the 7-*exo*-isomers **5a** (1-COOEt, 7-Ph) and **5b** (1-COOEt, 7-vinyl) appear at a similar region to the corresponding signals of **2a** (1-Ph, 7-Ph) and **2b** (1-Ph, 7-vinyl), while the 7-*endo*-isomers **6a** (1-COOEt, 7-Ph) and **6b** (1-COOEt, 7-vinyl) exhibited 6-H signals similar to those of **3a** (1-Ph, 7-Ph) and **3b** (1-Ph, 7-vinyl), respectively. Furthermore, the ^{13}C-NMR spectral data of the cyclobutanes (Table III) revealed that the chemical shifts of the 7-carbon are similar in both 1-phenyl and 1-ethoxycarbonyl cyclobutanes, if the stereochemistry of the 7-substituent is the same.

The chemical shifts of 6-H in **6d** and **6e** are coincident with those of the 7-*endo*-isomers **3d** and **3e** rather than those of the 7-*exo*-isomers **2d** and **2e**, respectively. The chemical shifts of the 7-carbon in **6d** and **6e** are also consistent with those of the *endo*-isomers **3d** and **3e**, respectively. Thus, the orientation of the 7-substituent in both **6d** and **6e** was concluded to be *endo*.

As described above, the photocycloaddition of **4** to isoprene yielded three adducts, **5f**, **6f**, and **7f**. The structures of these adducts were elucidated as follows. Pyrolyses of **5f** and **6f** gave the same product **7f**, a minor photoadduct. The spectral features of this compound revealed that it is the hydroindole regioisomeric to the Diels–Alder adduct **20** of **4** to isoprene.[8] Thus, **5f** and **6f** were established as 7-epimers of cyclobutanes. However, the application of the thermal reaction of the imidate to differentiate the stereochemistry of the 7-vinyl group was unsuccessful, since the imidation of **6f** with Meerwein reagent yielded a complex mixture and no characterizable product was isolated. On the other hand the imidate **16** prepared from **5f** on thermal reaction underwent two types of 1,3-rearrangement reactions which are characteristic of the 7-*exo* vinyl isomer[9] to yield the hydroindole **22** (48%) and the dihydropyridone **23** (49%), thus suggesting the vinyl group of **5f** to have *exo*-orientation.[10]

Furthermore, the stereochemistry of the 7-substituents was supported by examination of the ^{1}H-NMR spectra. We have observed that the 7-*endo*-Me isomers such as the 7-*exo*-Ac-7-*endo*-Me **24** and the *exo*-vinly-7-*endo*-Me **25** showed a long-range coupling between the 6-*exo*-H and 7-*endo*-Me, while the 7-*exo*-Me isomers such as **26** showed no such long-range coupling.[3] The major adduct **5f** showed a long-range coupling between 6-H and 7-Me, while the minor adduct **6f** gave no such long-range coupling, so the former was assigned as the *exo*-vinyl-*endo*-Me isomer and the latter as the *exo*-Me-*endo*-vinyl isomer.

Conclusion

In summary, the photocycloaddition of the 4,5-diCOOEt-dioxopyrroline **4** to electron-rich olefins proceeded in a regioselective manner to give [2+2] adducts with H-T regiochemistry. The stereochemistry of the adducts is dependent on the nature of the olefins. Olefins carrying *O*-substituents such as ethoxy and acetoxyl groups exclusively afforded the isomer **6** with *O*-*endo*-configuration, while olefins carrying phenyl and ethyl groups afforded the *exo*- (**5**) and *endo*- (**6**) isomers with an *exo*-preference, and butadiene gave the *exo*- (**5**) and *endo*- (**6**) isomers with slight *endo*-preference. The results showed a similar stereochemical tendency to the reactions of the 4-COOEt-5-Ph dioxopyrroline **1**, thus demonstrating that the replacement of a phenyl group by COOEt at the double bond of the dioxopyrroline ring scarcely affected the stereochemical pathway. Therefore, the polarity of the pair in the transition state was suggested to remain essentially unaltered, although

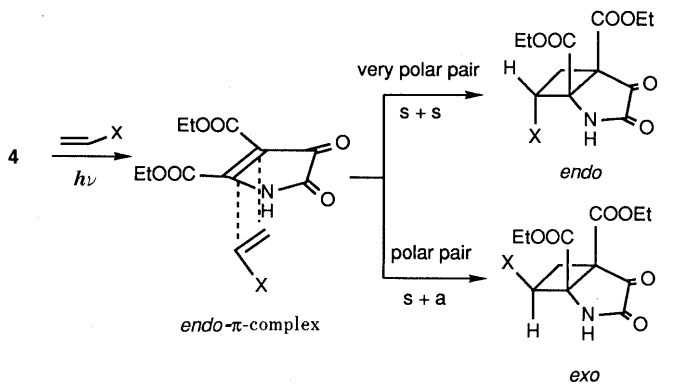


Chart 6

the increase of electrophilic character of the double bond caused by this replacement had an observable effect on the Diels–Alder reaction.[8]

This stereochemical result is also consistent with the stereo-selection rule of enone-olefin photocycloaddition.[4] This rule states that when the enone–olefin pair is very polar, the s+s pathway is predominant from the favored *endo*-π transition state, while the s+a addition is favored when the pair is polar. The *endo*-selectivity observed in the reactions of olefins carrying oxygen substituents and the *exo*-selectivity observed in styrene and 1-butene can be explained by considering that the former pairs are very polar, while the latter pairs are polar. The pair of butadiene or isoprene seems to be intermediate between the very polar and polar pairs. Thus, in the very polar pairs the addition proceeds preferentially in an s+s manner from the *endo*-π-complex as a favored transition state, and in the polar pairs the addition proceeds preferentially in an s+a manner from the favored transition state, thus giving rise to the *endo*- and *exo*-adducts, respectively.

Finally, it should be briefly mentioned that solvents affect the yield of the photocycloaddition of **4**, although they do not affect the stereochemical outcome. Benzene was a better solvent than DME (Table I). In the case of the 4-COOEt-5-Ph-dioxopyrroline **1**, DME gave a good result,[3] but benzene was not a suitable solvent, since the solubility of **1** in benzene was too poor to allow the reaction to be conducted. DME is more transparent to shorter wavelength light (<290 nm) than benzene is. This may result in further decomposition of the [2+2] adducts, leading to the lower yield, though we have no evidence for this as yet.

Experimental

Unless otherwise stated, the following procedures were adopted. Melting points were taken on a Yanagimoto micro hot-stage melting point apparatus and are uncorrected. IR spectra were taken in Nujol mulls for solids and CH_2Cl_2 solution for gums with a Hitachi 260-10 spectrometer and data are given in cm^{-1}. UV spectra were recorded in dioxane solution with a Hitachi 200-10 spectrometer and data are given in λ_{max} nm (ε). ^{1}H-NMR (100 MHz) and ^{13}C-NMR (25.0 MHz) spectra were taken in $CDCl_3$ solution with tetramethylsilane as an internal standard on a JEOL FX-100 spectrometer. High resolution mass spectra (HRMS) were recorded on a JEOL JMS-D300 mass spectrometer. For column chromatography, silica gel (Wako gel C-200) was used. Thin layer chromatography (TLC) was performed on Merck precoated Silica gel 60 F_{254} plates (Merck). Medium pressure liquid chromatography (MPLC) was performed on a Kusano CIG prepacked silica gel column. The photolysis was done by internal irradiation using a 300 W high-pressure mercury lamp (Eikosha Halos PIH 300) with a Pyrex filter. The preparation of **4** was carried out by the known method.[8]

Photocycloaddition of 4 with Olefins (General Procedure) A solution of **4** (2.0 g, 8 mmol) and an olefin (40 mmol) in benzene (300 ml) was irradiated at 0°C for 45—60 min. After removal of the solvent *in vacuo*, the residue in benzene was chromatographed. Elution with CH_2Cl_2–benzene (1 : 1) gave a mixture of the cyclobutanes **5** and **6**, which were separated by MPLC using AcOEt–hexane (1 : 1) as an eluent and fractional crystallizations from Et_2O–hexane. In the case of isoprene, three adducts **5f**, **6f**, and **7** were isolated by MPLC using AcOEt–hexane (1 : 1) as an eluent.

Styrene Photoadducts *dl*-(1*R**,5*R**,7*R**)-1,5-Diethoxycarbonyl-7-phenyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**5a**): 923 mg, 21%. Colorless prisms, mp 155—157 °C. IR: 1700, 1740, 1720. UV: 270 (3700). ^{1}H-NMR: 0.82 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.18 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.59 (1H, dd, J=9, 13 Hz, H-6), 3.43 (1H, dd, J=11, 13 Hz, H-6), 3.77 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 3.80 (1H, dd, J=9, 11 Hz, H-7), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 7.0 (2H, m, ArH), 7.3 (3H, m, ArH), 8.61 (1H, br s, NH). ^{13}C-NMR: 13.4 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 24.7 (t, C6), 52.5 (d, C7), 54.2 (s, C5), 62.1 (t, $COO\underline{C}H_2CH_3$), 62.4 (t, $COO\underline{C}H_2CH_3$), 68.9 (s, C1), 127.0 (d, 2C, Ph), 127.9 (d, Ph), 128.6 (d, 2C, Ph), 136.0 (s, Ph), 160.7 (s, C3), 165.0 (s, $\underline{C}OOCH_2CH_3$), 165.6 (s, $\underline{C}OOCH_2CH_3$), 194.7 (s, C4). *Anal.* Calcd for $C_{18}H_{19}NO_6$: C, 62.60; H, 5.55; N, 4.06. Found: C, 62.35; H, 5.45; N, 4.12. HRMS m/z (M^+): 345.1212. Found: 345.1232.

dl-(1*R**,5*R**,7*S**)-1,5-Diethoxycarbonyl-7-phenyl-2-azabicyclo[3.2.0]-heptane-3,4-dione (**6a**): 497 mg, 12%. Colorless prisms, mp 119—122 °C. IR: 1780, 1750, 1730. UV: 213 (10700). ^{1}H-NMR: 1.26 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.48 (1H, dd, J=9, 13 Hz, H-6), 3.36 (1H, dd, J=10, 13 Hz, H-6), 4.15—4.35 (4H, m, $2COOC\underline{H}_2CH_3$), 4.53 (1H, dd, J=9, 10 Hz, H-7), 7.0 (2H, m, ArH), 7.3 (3H, m, ArH), 8.61 (1H, br s, NH). ^{13}C-NMR: 14.0 (q, $COOCH_2\underline{C}H_3$), 14.1 (q, $COOCH_2\underline{C}H_3$), 27.0 (t, C6), 43.4 (d, C7), 54.3 (s, C5), 62.7 (t, $COO\underline{C}H_2CH_3$), 63.0 (t, $COO\underline{C}H_2CH_3$), 64.9 (s, C1), 127.7 (d, 2C, Ph), 128.0 (d, 3C, Ph), 134.9 (s, Ph), 160.5 (s, C3), 165.4 (s, $\underline{C}OOCH_2CH_3$), 167.9 (s, $\underline{C}OOCH_2CH_3$), 192.7 (s, C4). *Anal.* Calcd for $C_{18}H_{19}NO_6$: C, 62.60; H, 5.55; N, 4.06. Found: C, 62.44; H, 5.63; N, 4.02. HRMS m/z (M^+): 345.1211. Found: 345.1216.

Butadiene Photoadducts *dl*-(1*R**,5*R**,7*R**)-1,5-Diethoxycarbonyl-7-vinyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**5b**): 433 mg, 18%. Colorless gum. IR: 1770, 1735. UV: 268 (2300). ^{1}H-NMR: 1.20 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.30 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.40 (1H, dd, J=8, 11 Hz, H-6), 2.84—3.13 (2H, m, H-6, H-7), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.26 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.11—5.31 (2H, m, $CH=C\underline{H}_2$), 5.69—6.03 (1H, m, $C\underline{H}=CH_2$), 9.29 (1H, br s, NH). ^{13}C-NMR: 14.0 (q, $COOCH_2\underline{C}H_3$), 14.1 (q, $COOCH_2\underline{C}H_3$), 26.2 (t, C6), 50.4 (d, C7), 54.2 (s, C5), 62.4 (t, 2C, $COO\underline{C}H_2CH_3$), 67.5 (s, C1), 119.4 (t, $CH=\underline{C}H_2$), 133.4 (d, $\underline{C}H=CH_2$), 160.3 (s, C3), 165.0 (s, $\underline{C}OOCH_2CH_3$), 165.8 (s, $\underline{C}OOCH_2CH_3$), 194.6 (s, C4). HMRS m/z Calcd for $C_{14}H_{17}NO_6$ (M^+): 295.1054. Found: 295.1032.

dl-(1*R**,5*R**,7*S**)-1,5-Diethoxycarbonyl-7-vinyl-2-azabicyclo[3.2.0]-heptane-3,4-dione (**6b**): 465 mg, 19%. Colorless prisms, mp 100—103 °C. IR: 1770, 1730. UV: 259 (3000). ^{1}H-NMR: 1.23 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.20 (1H, dd, J=8, 13 Hz, H-6), 3.23 (1H, dd, J=10, 13 Hz, H-6), 3.80 (1H, dd, J=8, 10 Hz, H-7), 4.20 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.27 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.04—5.36 (2H, m, $CH=C\underline{H}_2$), 5.60—5.94 (1H, m, $C\underline{H}=CH_2$), 8.64—8.92 (1H, br s, NH). ^{13}C-NMR: 14.0 (q, 2C, $COOCH_2\underline{C}H_3$), 26.8 (t, C6), 42.3 (d, C7), 54.6 (s, C5), 62.6 (t, $COO\underline{C}H_2CH_3$), 62.8 (t, $COO\underline{C}H_2CH_3$), 64.5 (s, C1), 119.9 (t, $CH=\underline{C}H_2$), 132.6 (d, $\underline{C}H=CH_2$), 161.2 (s, C3), 165.2 (s, $\underline{C}OOCH_2CH_3$), 167.7 (s, $\underline{C}OOCH_2CH_3$), 193.2 (s, C4). *Anal.* Calcd for $C_{14}H_{17}NO_6$: C, 56.94; H, 5.80; N, 4.74. Found: C, 56.65; H, 5.66; N, 4.68. HRMS m/z (M^+): 295.1054. Found: 295.1018.

1-Butene Photoadducts *dl*-(1*R**,5*R**,7*S**)-1,5-Diethoxycarbonyl-7-ethyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**5c**): 761 mg, 21%. Colorless gum. IR(CH_2Cl_2): 1770, 1735. UV: 265 (2000). ^{1}H-NMR: 0.73 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.12 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.26 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.31—1.59 (2H, m, $C\underline{H}_2CH_3$), 2.15—2.56 (3H, m, H-6, H-7), 4.08 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.18 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 9.26 (1H, br s, NH). ^{13}C-NMR: 11.0 (q, $CH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 14.1 (q, $COOCH_2\underline{C}H_3$), 24.0 (t, $\underline{C}H_2CH_3$), 27.2 (t, C6), 49.8 (d, C7), 54.3 (s, C5), 62.4 (t, 2C, $COO\underline{C}H_2CH_3$), 66.0 (s, C1), 160.4 (s, C3), 165.3 (s, $\underline{C}OOCH_2CH_3$), 166.4 (s, $\underline{C}OOCH_2CH_3$), 195.0 (s, C4). HRMS m/z Calcd for $C_{14}H_{19}NO_6$ (M^+): 297.1212. Found: 297.1222.

dl-(1*R**,5*R**,7*R**)-1,5-Diethoxycarbonyl-7-ethyl-2-azabicyclo[3.2.0]-heptane-3,4-dione (**6c**): 422 mg, 12%. Colorless prisms, mp 133—135 °C.

IR: 1760, 1730, 1715. UV: 258 (2900). ^{1}H-NMR: 0.77 (3H, t, J=7 Hz, $CH_2C\underline{H}_3$), 1.14 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.24 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.26—1.79 (3H, m, $C\underline{H}_2CH_3$, H-6), 2.95—3.22 (2H, m, H-6, H-7), 4.10 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.12 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 8.96 (1H, br s, NH). ^{13}C-NMR: 10.7 (q, $CH_2\underline{C}H_3$), 13.9 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 23.1 (t, $\underline{C}H_2CH_3$), 28.4 (t, C6), 41.7 (d, C7), 54.6 (s, C5), 62.5 (t, $COO\underline{C}H_2CH_3$), 62.7 (t, $COO\underline{C}H_2CH_3$), 63.8 (s, C1), 161.2 (s, C3), 165.3 (s, $\underline{C}OOCH_2CH_3$), 168.5 (s, $\underline{C}OOCH_2CH_3$), 193.5 (s, C4). *Anal.* Calcd for $C_{14}H_{19}NO_6$: C, 56.56; H, 6.44; N, 4.71. Found: C, 56.66; H, 6.24; N, 4.55. HRMS m/z (M^+): 297.1211. Found: 297.1201.

Ethoxyethylene Photoadduct *dl*-(1*R**,5*R**,7*R**)-7-Ethoxy-1,5-diethoxycarbonyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**6d**): 1081 mg, 28%. Colorless prisms, mp 113—115 °C. IR: 1780, 1760, 1730. UV: 259 (3100). ^{1}H-NMR: 1.16 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.22 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.13 (1H, dd, J=5, 14 Hz, H-6), 3.29 (1H, dd, J=8, 14 Hz, H-6), 3.45 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.18 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.28 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.46 (1H, dd, J=5, 8 Hz, H-7), 7.45 (1H, br s, NH). ^{13}C-NMR: 14.0 (q, 2C, $COOCH_2\underline{C}H_3$), 14.8 (q, $OCH_2\underline{C}H_3$), 32.3 (t, C6), 53.2 (s, C5), 62.6 (t, $COO\underline{C}H_2CH_3$), 62.8 (t, $COO\underline{C}H_2CH_3$), 63.8 (s, C1), 65.7 (t, $O\underline{C}H_2CH_3$), 74.0 (d, C7), 161.6 (s, C3), 165.1 (s, $\underline{C}OOCH_2CH_3$), 167.6 (s, $\underline{C}OOCH_2CH_3$), 192.6 (s, C4). *Anal.* Calcd for $C_{14}H_{19}NO_7$: C, 53.67; H, 6.11; N, 4.47. Found: C, 53.45; H, 6.22; N, 4.53. HRMS m/z (M^+): 313.1160. Found: 313.1140.

Acetoxyethylene Photoadduct *dl*-(1*R**,5*R**,7*R**)-7-Acetoxy-1,5-diethoxycarbonyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**6e**): 1543 mg, 38%. Colorless needles, mp 113—117 °C. IR: 1775, 1745, 1730. UV: 256 (3100). ^{1}H-NMR: 1.22 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.33 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.12 (3H, s, $COCH_3$), 2.33 (1H, dd, J=6, 14 Hz, H-6), 3.45 (1H, dd, J=9, 14 Hz, H-6), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.32 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.29 (1H, dd, J=6, 9 Hz, H-7), 8.24 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.0 (q, $COOCH_2\underline{C}H_3$), 20.3 (q, $OCO\underline{C}H_3$), 29.7 (t, C6), 53.3 (s, C5), 62.9 (t, $COO\underline{C}H_2CH_3$), 63.0 (t, $COO\underline{C}H_2CH_3$), 65.0 (s, C1), 68.7 (d, C7), 160.3 (s, C3), 164.5 (s, $\underline{C}OOCH_2CH_3$), 166.6 (s, $\underline{C}OOCH_2CH_3$), 170.9 (s, $\underline{C}OCH_3$), 192.0 (s, C4). *Anal.* Calcd for $C_{14}H_{17}NO_8$: C, 51.37; H, 5.24; N, 4.28. Found: C, 51.52; H, 5.33; N, 4.12. HRMS m/z (M^+): 327.0952. Found: 327.0942.

Isoprene Photoadducts *dl*-(1*R**,5*R**,7*R**)-1,5-Diethoxycarbonyl-7-methyl-7-vinyl-2-azabicyclo[3.2.0]heptane-3,4-dione (**5f**): 1007 mg, 26%. Colorless prisms, mp 84—88 °C. IR: 1775, 1740. UV: 268 (2800). ^{1}H-NMR: 1.12 (3H, s, CH_3), 1.19 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.28 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.00 (1H, d, J=13 Hz, H-6), 3.20 (1H, d, J=13 Hz, H-6), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.22 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.18 (1H, d, J=18 Hz, $CH=C\underline{H}_2$), 5.20 (1H, d, J=10 Hz, $CH=C\underline{H}_2$), 5.89 (1H, dd, J=10, 18 Hz, $C\underline{H}=CH_2$), 8.85 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.1 (q, $COOCH_2\underline{C}H_3$), 22.9 (q, CH_3), 34.4 (t, C6), 47.8 (s, C7), 53.0 (s, C5), 62.3 (t, $COO\underline{C}H_2CH_3$), 62.4 (t, $COO\underline{C}H_2CH_3$), 68.5 (s, C1), 116.2 (t, $CH=\underline{C}H_2$), 139.0 (d, $\underline{C}H=CH_2$), 161.2 (s, C3), 165.2 (s, $\underline{C}OOCH_2CH_3$), 166.2 (s, $\underline{C}OOCH_2CH_3$), 194.4 (s, C4). *Anal.* Calcd for $C_{15}H_{19}NO_6$: C, 58.24; H, 6.19; N, 4.53. Found: C, 58.45; H, 6.06; N, 4.55. HRMS m/z (M^+): 309.1212. Found: 309.1219.

dl-(1*R**,5*R**,7*S**)-1,5-diethoxycarbonyl-7-methyl-7-vinyl-2-azabicyclo-[3.2.0]heptane-3,4-dione (**6f**): 576 mg, 15%. Colorless prisms, mp 83—87 °C. IR: 1780, 1740. UV: 264 (2300). ^{1}H-NMR: 1.20 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.33 (3H, s, CH_3), 1.35 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.45 (1H, d, J=13 Hz, H-6), 2.84 (1H, d, J=13 Hz, H-6), 4.18 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.32 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.03 (1H, d, J=17 Hz, $CH=C\underline{H}_2$), 5.30 (1H, d, J=10 Hz, $CH=C\underline{H}_2$), 5.73 (1H, dd, J=10, 17 Hz, $C\underline{H}=CH_2$), 8.75 (1H, br s, NH). ^{13}C-NMR: 13.9 (q, $COOCH_2\underline{C}H_3$), 14.1 (q, $COOCH_2\underline{C}H_3$), 23.2 (q, CH_3), 31.8 (t, C6), 48.6 (s, C7), 52.7 (s, C5), 62.4 (t, $COO\underline{C}H_2CH_3$), 62.5 (t, $COO\underline{C}H_2CH_3$), 67.9 (s, C1), 117.5 (t, $CH=\underline{C}H_2$), 138.6 (d, $\underline{C}H=CH_2$), 161.3 (s, C3), 165.6 (s, $\underline{C}OOCH_2CH_3$), 166.1 (s, $\underline{C}OOCH_2CH_3$), 194.6 (s, C4). *Anal.* Calcd for $C_{15}H_{19}NO_6$: C, 58.24; H, 6.19; N, 4.53. Found: C, 58.12; H, 6.03; N, 4.45. HRMS m/z (M^+): 309.1212. Found: 309.1220.

dl-(1*R**,6*R**)-1,6-Diethoxycarbonyl-3-methyl-7-azabicyclo[4.3.0]-nona-3-ene-8,9-dione (**7**): 136 mg, 4%. Colorless prisms, mp 118—124 °C. IR: 1790, 1750. UV: 253 (3100). ^{1}H-NMR: 1.18 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.31 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.74 (3H, s, CH_3), 2.53—2.94 (4H, m, 2-H and 5-H), 4.18 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.19 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.25—5.52 (1H, m, 4-H), 9.30—9.55 (1H, br s, NH). ^{13}C-NMR: 13.7 (q, $COOCH_2\underline{C}H_3$), 13.9 (q, $COOCH_2\underline{C}H_3$), 23.1 (q, CH_3), 32.3 (t, C2 or C5), 35.7 (t, C2 or C5), 60.2 (s, C1), 62.5 (t, $COO\underline{C}H_2CH_3$), 62.6 (t, $COO\underline{C}H_2CH_3$), 65.2 (s, C6), 117.8 (d, C3 or C4), 138.8 (d, C3 or C4), 159.0 (s, C8), 165.9 (s, $\underline{C}OOCH_2CH_3$), 170.5 (s, $\underline{C}OOCH_2CH_3$), 195.3 (s, C9). *Anal.* Calcd for $C_{15}H_{19}NO_6$: C, 58.24; H, 6.19; N, 4.53. Found: C, 58.15; H, 5.96; N, 4.35. HRMS m/z (M^+): 309.1212. Found: 309.1248.

Treatment of 6a with DBU A mixture of **6a** (150 mg) and DBU (300 mg) in benzene (15 ml) was stirred for 2 d at room temperature. The reaction mixture was diluted with CH_2Cl_2. The organic layer was washed with 5% HCl and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in CH_2Cl_2 was chromatographed over SiO_2 to give 4,7-diethoxycarbonyl-3-hydroxy-6-phenyl-1,5-dihydro-2*H*-azepin-2-one (**8**) (38 mg, 25%) as colorless prisms from Et_2O, mp 203—205 °C. IR: 3230, 1740, 1690, 1660. UV: 317 (9600). ^{1}H-NMR: 0.86 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.16 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 3.34 (2H, s, H-5), 3.90—4.14 (4H, m, $2COOC\underline{H}_2CH_3$), 7.06—7.42 (5H, m, ArH). HRMS m/z Calcd for $C_{18}H_{19}NO_6$ (M^+): 345.1213. Found: 345.1213.

Imidation of 5a and 6a with Triethyloxonium Fluoroborate A mixture of **5a** or **6a** (each 150 mg) and a large excess of Et_3OBF_4 in CH_2Cl_2 (7 ml) was stirred at room temperature overnight. The reaction mixture was diluted with CH_2Cl_2. The organic layer was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in benzene was chromatographed over SiO_2 (CC-7) to give the imidate **9** (73 mg, 45%) or **10** (93 mg, 57%).

dl-(1*R**,5*R**,7*R**)-3-Ethoxy-1,5-diethoxycarbonyl-7-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-dione (**9**): Colorless prisms from Et_2O–hexane, mp 86—89 °C. IR: 1745, 1725, 1620. UV: 260 (4200). ^{1}H-NMR: 0.75 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.20 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.55 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.25 (1H, dd, J=9, 13 Hz, H-6), 3.40 (1H, dd, J=11, 13 Hz, H-6), 3.70—3.90 (1H, m, H-7), 3.75 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.15 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.40 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.25—7.40 (5H, m, ArH). HRMS m/z Calcd for $C_{20}H_{23}NO_6$ (M^+): 373.1525. Found: 373.1515.

dl-(1*R**,5*R**,7*S**)-3-Ethoxy-1,5-diethoxycarbonyl-7-phenyl-2-azabicyclo[3.2.0]hept-2-en-4-dione (**10**): Colorless gum. IR: 1750, 1730, 1615. ^{1}H-NMR: 1.05 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.25 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.35 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.25 (1H, dd, J=9, 10 Hz, H-6), 3.30 (1H, dd, J=10, 13 Hz, H-6), 4.20 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.25 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.35 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 4.65 (1H, dd, J=9, 13 Hz, H-7), 6.95—7.50 (5H, m, ArH). HRMS m/z Calcd for $C_{20}H_{23}NO_6$ (M^+): 373.1526. Found: 373.1559.

Pyrolysis of 9 and 10 A solution of **9** (60 mg) or **10** (79 mg) in *p*-cymene (3 ml) was heated in a sealed tube (250 °C, 5 h for **9** and 300 °C, 9 h for **10**). After removal of the solvent by evaporation *in vacuo*, the residue was purified by chromatography over SiO_2 (CC-7) (solvent, CH_2Cl_2) and by PTLC (solvent, AcOEt–hexane (3 : 2)) to give **11** (12 mg, 24% from **9** and 4 mg, 1% from **10**) and **12** (6 mg, 11% from **9** and 20 mg, 27% from **10**).

5,6-Diethoxycarbonyl-3-phenyl-3,4-dihydropyridin-2(1*H*)-one (**11**): Colorless prisms from Et_2O–hexane, mp 89—90 °C. IR: 1745, 1700, 1685, 1645. UV; 282 (9500). ^{1}H-NMR: 1.31 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.32 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.98 (1H, d, J=10 Hz, H-4), 2.99 (1H, d, J=8 Hz, H-4), 3.79 (1H, dd, J=8, 10 Hz, H-3), 4.25 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.30 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 7.32—7.36 (5H, m, ArH), 7.73 (1H, br s, NH). HRMS m/z Calcd for $C_{17}H_{19}NO_5$ (M^+): 317.1261. Found: 317.1350.

2-Ethoxy-5,6-diethoxycarbonyl-3-phenylpyridine (**12**): Colorless prisms from Et_2O–hexane, mp 96—98 °C. IR: 1740, 1715. UV: 229 (16900), 283 (9200). ^{1}H-NMR: 1.36 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.37 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.42 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 4.36 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.46 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.52 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 7.28—7.64 (5H, m, ArH), 8.17 (1H, s, H-4). HRMS m/z Calcd for $C_{19}H_{21}NO_5$ (M^+): 343.1420. Found: 343.1450.

Pyrolysis of 5b and 6b A solution of **5b** (200 mg) or **6b** (103 mg) in xylene (10 ml) was heated in a sealed tube (200 °C, 5 h for **5b** and 250 °C, 3 h for **6b**). After removal of the solvent by evaporation *in vacuo*, the residue in CH_2Cl_2 was chromatographed to give *dl*-(1*R**,6*R**)-1,6-diethoxycarbonyl-7-azabicyclo[4.3.0]nona-3-ene-8,9-dione (**15**) (11 mg, 13% from **5b** and 21 mg, 20% from **6b**) as colorless prisms from Et_2O–hexane, mp 138—140 °C. IR: 1780, 1740. UV: 254 (3100). ^{1}H-NMR: 1.18 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.31 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.50—2.67 (3H, m, H-2, H-5), 2.91—3.13 (1H, m, H-2 or H-5), 4.17 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.20 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.75—6.06 (2H, m, H-3, H-4), 9.08 (1H, br s, NH). HRMS m/z Calcd for $C_{14}H_{17}NO_6$ (M^+): 295.1056. Found: 295.1094.

Imidation of 5b with Et_3OBF_4 A mixture of **5b** (100 mg) and a large

excess of Et_3OBF_4 in CH_2Cl_2 (6 ml) was stirred for 4 h at room temperature. The reaction mixture was extracted with CH_2Cl_2. The organic extract was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in benzene was chromatographed over SiO_2(CC-7) to give *dl*-(1*R**,5*R**,7*R**)-3-ethoxy-1,5-diethoxycarbonyl-7-vinyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**16**) (90 mg, 83%). Colorless gum. IR (CH_2Cl_2): 1765, 1745, 1630. UV: 255 (3400). ^{1}H-NMR: 1.12 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.21 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.40 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.06 (1H, dd, J=8, 12 Hz, H-6), 2.53—3.00 (2H, m, H-6, H-7), 4.09 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.46 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.20—5.24 (2H, m, $CH=C\underline{H}_2$), 5.72—6.06 (1H, m, $C\underline{H}=CH_2$). HRMS *m/z* Calcd for $C_{16}H_{21}NO_6$ (M^+): 323.1369. Found: 323.1400.

Treatment of 6b with Et_3OBF_4 A mixture of **6b** (120 mg) and a large excess of Et_3OBF_4 in CH_2Cl_2 (6 ml) was stirred for 4 h at room temperature. The reaction mixture was extracted with CH_2Cl_2. The organic extract was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in benzene was chromatographed over SiO_2 (CC-7) to give *dl*-(1*R**,4*R**)-1-ethoxy-3,4-diethoxycarbonyl-2-azabicyclo[4.2.1]nona-2,6-dien-9-one **19** (117 mg, 89%). Colorless gum. IR (CH_2Cl_2): 1785, 1750, 1725, 1625. UV: 240 sh (1200). ^{1}H-NMR: 1.22 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.25 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.38 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.70—1.76 (1H, m, H-5 or H-8), 2.43—2.96 (3H, dd, m, H-5, H-8), 3.51 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.23 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.39 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.30—5.52 (2H, m, H-6, H-7). HRMS *m/z* Calcd for $C_{16}H_{21}NO_6$ (M^+): 323.1367. Found: 323.1362.

Pyrolysis of 16 A solution of **16** (55 mg) in toluene (6 ml) was heated in a sealed tube at 200 °C for 3 h. After removal of the solvent by evaporation *in vacuo*, the residue was purified by PTLC (solvent, AcOEt–hexane (1 : 3)) to give **17** (16 mg, 29%) and **19** (5 mg, 9%).

dl-(1*R**,6*R**)-8-Ethoxy-1,6-diethoxycarbonyl-7-azabicyclo[4.3.0]nona-3,7-dien-9-one (**17**): Colorless gum. IR (CH_2Cl_2): 1770, 1745, 1645. UV: 240 (3600). ^{1}H-NMR: 1.17 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.29 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.41 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 2.64—2.79 (4H, m, H-2, H-5), 4.13 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.42 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.72—5.90 (2H, m, H-3, H-4). HRMS *m/z* Calcd for $C_{16}H_{21}NO_6$ (M^+): 323.1369. Found: 323.1372.

Imidation of 15 with Et_3OBF_4 A mixture of **15** (100 mg) and a large excess of Et_3OGF_4 in CH_2Cl_2 (6 ml) was stirred for 6 h at room temperature. The reaction mixture was extracted with CH_2Cl_2. The organic extract was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in benzene was chromatographed over SiO_2 (CC-7) to give **17** (107 mg, 98%) as a colorless gum.

Catalytic Hydrogenation of 5b and 6b A solution of **5b** or **6b** (each 100 mg) in EtOH (10 ml) was hydrogenated over 5% Pd–C (100 mg) at room temperature for 2.5 h. After removal of the catalyst by filtration, the filtrate was concentrated to dryness *in vacuo*. The residue was chromatographed over SiO_2 (CC-7) (solvent, CH_2Cl_2) to give **5c** (57 mg, 56%) as a colorless gum or **6c** (47 mg, 47%) as colorless prisms from Et_2O–hexane, mp 133—135 °C.

Pyrolysis of 5f and 6f A solution of **5f** (44 mg) or **6f** (41 mg) in toluene (7 ml) was heated in a sealed tube (200 °C, 5 h for **5f** and 200 °C, 10 h for **6f**). After removal of the solvent by evaporation *in vacuo*, the residue was purified by PTLC (solvent, AcOEt–hexane (3 : 2)) to give **7** (16 mg, 36% from **5f** and 7 mg, 17% from **6f**).

Imidation of 5f with Et_3OBF_4 A mixture of **5f** (140 mg) and a large excess of Et_3OBF_4 in CH_2Cl_2 (10 ml) was stirred for 4 h at room temperature. The reaction mixture was extracted with CH_2Cl_2. The organic extract was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in benzene was chromatographed over SiO_2 (CC-7) to give *dl*-(1*R**,5*R**,7*R**)-3-ethoxy-1,5-diethoxycarbonyl-7-methyl-7-vinyl-2-azabicyclo[3.2.0]hept-2-en-4-one (**21**) (110 mg, 73%). Colorless gum. IR (CH_2Cl_2): 1750, 1730, 1615. UV: 257 (3500). ^{1}H-NMR: 0.98 (3H, s, 7-CH_3), 1.20 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.26 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.48 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.71 (1H, d, J=13 Hz, H-6), 3.18 (1H, d, J=13 Hz, H-6), 4.16 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.20 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.55 (2H, q, J=7 Hz, $OC\underline{H}_2CH_3$), 5.19 (1H, d, J=11 Hz, $CH=C\underline{H}_2$), 5.22 (1H, d, J=18 Hz, $CH=C\underline{H}_2$), 6.06 (1H, dd, J=11, 18 Hz, $C\underline{H}=CH_2$). HRMS *m/z* $C_{17}H_{23}NO_6$ (M^+): 337.1522. Found: 337.1490.

Pyrolysis of 21 A solution of **21** (91 mg) in toluene (6 ml) was heated in a sealed tube at 160 °C for 2 h. After removal of the solvent by evaporation *in vacuo*, the residue was chromatographed over SiO_2 (CC-7) (solvent, benzene–hexane (1 : 1)) to give **22** (44 mg, 48%) and **23** (37 mg, 49%).

dl-(1*R**,6*R**)-8-Ethoxy-1,6-diethoxycarbonyl-3-methyl-7-azabicyclo-[4.3.0]-nona-3,7-dien-9-one (**22**): Colorless gum. IR (CH_2Cl_2): 1755, 1735, 1630. UV: 239 (3400). ^{1}H-NMR: 1.09 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.22 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.34 (3H, t, J=7 Hz, $OCH_2C\underline{H}_3$), 1.62 (3H, s, CH_3), 2.57 (4H, m, H-2, H-5), 4.06 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.09 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.36 (2H, qd, J=4, 7 Hz, $OC\underline{H}_2CH_3$), 5.25 (1H, m, H-4). HRMS *m/z* Calcd for $C_{17}H_{23}NO_6$ (M^+): 337.1526. Found: 337.1559.

5,6-Diethoxycarbonyl-3-methyl-3-vinyl-3,4-dihydropyridin-2(1*H*)-one (**23**): Colorless gum. IR (CH_2Cl_2): 1730, 1690, 1615. UV: 289 (4700). ^{1}H-NMR: 1.26 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 1.27 (3H, s, CH_3), 1.34 (3H, t, J=7 Hz, $COOCH_2C\underline{H}_3$), 2.38 (1H, d, J=18 Hz, H-4), 2.69 (1H, d, J=18 Hz, H-4), 4.25 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 4.29 (2H, q, J=7 Hz, $COOC\underline{H}_2CH_3$), 5.03 (1H, d, J=17 Hz, $CH=C\underline{H}_2$), 5.07 (1H, d, J=11 Hz, $CH=C\underline{H}_2$), 5.77 (1H, dd, J=11, 17 Hz, $C\underline{H}=CH_2$), 7.32 (1H, br s, NH). HRMS *m/z* Calcd for $C_{14}H_{19}NO_5$ (M^+): 281.1211. Found: 281.1239.

Imidation of 7 with Et_3OBF_4 A mixture of **7** (35 mg) and a large excess of Et_3OBF_4 in CH_2Cl_2 (6 ml) was stirred overnight at room temperature. The reaction mixture was extracted with CH_2Cl_2. The organic extract was washed with 5% $NaHCO_3$ and water, dried over Na_2SO_4, and concentrated to dryness *in vacuo*. The residue in benzene was chromatographed over SiO_2 (CC-7) to give **22** (32 mg, 76%) as a colorless gum.

References and Notes

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