2 H, $C_\beta H_2$), 1.42 (s, 9 H, $(CH_3)_3C$).

Anal. Calcd for $C_{15}H_{22}N_2O_4$: C, 61.21; H, 7.53; N, 9.52. Found: 61.39; H, 7.68; N, 9.36.

Methyl *N*-(*N*-(*tert*-Butyloxycarbonyl)-1-amino-2-phenylethyl)allophanate (7c): yield 12%; R_{f_1} 0.26; mp 157-159 °C; $[\alpha]^{23}_D$ +12.0° (c 3.0, DMF); IR (KBr) 1733, 1692, 1557, 1498 cm^{-1}; NMR ($CDCl_3$) δ 8.29 (d, 1 H, $C_\alpha H$-N*H*-CO), 7.45 (s, 1 H, CO-NH-CO), 7.23 (m, 5 H, Ar), 5.41 (m, 1 H, $C_\alpha H$), 5.27 (m, 1 H, Boc-*NH*), 3.75 (s, 3 H, OCH_3), 3.15 (d, 2 H, $C_\beta H_2$), 1.42 (s, 9 H, $(CH_3)_3C$).

Anal. Calcd for $C_{16}H_{23}N_3O_5$: C, 56.96, H, 6.87; N, 12.45. Found: C, 57.00; H, 6.93; N, 12.50.

(b) Ratio of Isocyanate to Alcohol 1:2. The amino acid derivative Boc-Phe-OH (20 mmol) was converted to the corresponding isocyanate (**2b**). Dry methanol (40 mmol) was added. After complete disappearance of isocyanate the mixture was taken to dryness and the residue was chromatographed on a silica gel column (2 × 30 cm) as described above. The products obtained are listed in order of their elution.

***N*-(*tert*-Butyloxycarbonyl)-*N'*-methoxycarbonyl-1,1-diamino-2-phenylethane (3c)**: yield 44.7%. Identical with the *gem*-diaminoalkyl compound described above.

Methyl *N*-(*N*-(*tert*-Butyloxycarbonyl)-1-aminophenethyl)allophanate (7c): yield 3.8%. Identical with the allophanate described above.

Reaction of *N*-Acetyl-*N'*-carbonyl-1,1-diamino-2-phenylethane (2d) with Methanol. (a) Ratio of Isocyanate to Alcohol 1:10. The compound *N*-acetylphenylalanine[23] (10 mmol) was converted to azide **1d**, taken up in 10 mL of dioxane, and rearranged to the isocyanate **2d**. Methanol (10 equiv) was added and after 90 min all of the isocyanate was consumed. Upon cooling at room temperature, the urethane crystallized from solution. An analytical sample recrystallized from MeOH yielded the desired diacylated *gem*-diaminoalkyl compound.

***N*-Acetyl-*N'*-(methyloxycarbonyl)-1,1-diamino-2-phenylethane (3d)**: yield 70%; R_{f_2} 0.52; mp 202-203 °C; $[\alpha]^{23}_D$ +3.88° (c 1.1, DMF); IR (KBr) 3300, 1698, 1648, 1555 cm^{-1}; NMR ($CDCl_3$) δ 7.30 (m, 5 H, Ar), 6.35 (m, 1 H, NH) 5.65 (m, 1 H, NH), 5.25 (m, 1 H, $C_\alpha H$), 3.66 (s, 3 H, CO_2CH_3), 3.20 (d, 2 H, J = 6.6 Hz, $C_\beta H_2$), 1.94 (s, 3 H, CH_3CONH).

Anal. Calcd for $C_{12}H_{16}N_2O_3$: C, 61.00; H, 6.83; N, 11.86. Found: C, 60.96; H, 6.90; N, 11.94.

The filtrate was taken to dryness and the residue chromatographed on a silica gel column (2 × 30 cm) with EtOAc-hexanes (1:1). The products obtained are reported in order of their elution:

***N*-Acetyl-1-amino-1-methoxy-2-phenylethane (4d)**: yield 2%; R_{f_3} 0.33; mp 98-99 °C (after recrystallization from EtOAc-hexane); $[\alpha]^{23}_D$ -0.3 (c 2.02, EtOH); IR (KBr) 3300, 1655, 1540, 1115 cm^{-1}; NMR ($CDCl_3$) δ 7.25 (m, 5 H, Ar), 5.58 (br d, 1 H, NH), 5.38 (m, 1 H, CH) 3.33 (s, 3 H, OCH_3), 2.92 (d, 2 H, J = 6.6 Hz, $PhCH_2$-), 1.96 (s, 3 H, CH_3CONH).

Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.18; H, 7.93; N, 7.08.

***N*-Acetyl-*N'*-(methyloxycarbonyl)-1,1-diamino-2-phenylethane (3d)**: Yield 6%. This material was identical with that obtained from the first crystallization.

(b) Ratio of Isocyanate to Alcohol 1:20. The substance *N*-acetylphenylalanine (10 mmol) was converted to the isocyanate **2d** by the general procedure already described and then subjected to one of the following conditions: 20 equiv of MeOH; 20 equiv of MeOH and 1 equiv of pyridine; 20 equiv of pyridine; 20 equiv of MeOH and 0.1 equiv of *p*-toluenesulfonic acid; 10 equiv of MeOH in dioxane; and the isocyanate solution in toluene added to refluxing MeOH (120 equiv). In all cases, the urethane crystallized from the reaction solution and was removed by filtration. The filtrate was taken to dryness and examined by Fourier Transform 220-MHz NMR to determine the extent of formation of 1-amino-1-methoxyalkyl compound (**4d**). These data are summarized in Table II.

***N*-(Benzyloxycarbonyl)-2-(*tert*-butyloxy)pyrrolidine (11).** The amino acid derivative Z-Pro-OH was converted to the corresponding isocyanate (**8**) and reacted with *t*-BuOH as described in the literature.[21] After 2 h of heating, all of the isocyanate was consumed (determined by IR). The solvent was removed under reduced pressure to yield a clear oil which was chromatographed on a silica gel column (2 × 30 cm) with EtOAc-hexane (1:1). The first fraction was obtained as a colorless oil: F_{f_1} 0.6; IR (neat) no NH, 1706 cm^{-1} (urethane C=O); NMR ($CDCl_3$) δ 7.34 (m, 5 H, Ar), 5.39 (br d, 1 H, $C_\alpha H$), 5.13 (m, 2 H, $PhCH_2O$-), 3.56 (m, 1 H, $C_\delta H$), 3.30 (m, 1 H, C-$C_\delta H$), 2.09 and 1.81 (m, 4 H, $C_\beta H_2$ and $C_\gamma H_2$), 1.28 and 1.13 (br d, br d, total of 9 H, 3:2, $(CH_3)_3C$); MS, *m/e* 277 (M^+), 221 ($M^+ - C_4H_8$), 205 ($M^+ - C_4H_8O$). The compound was not sufficiently stable to be sent for elemental analysis. The latter fractions were found to correspond to the gem-diaminoalkyl compound (**9**) and the allophanate (**10**) described by Murato et al.[21]

Acknowledgment. The ^1H spectra were obtained on the 220-MHz NMR spectrometer at the UCSD NMR/MS Research Resource (NIH Grant RR 00708). Our research was supported by NIH Grant AM 15410.

Registry No. **1d**, 18934-58-2; **2a**, 88425-14-3; **2b**, 88425-15-4; **2d**, 88425-16-5; **3a**, 88425-17-6; **3b**, 88425-18-7; **3c**, 88425-19-8; **3d**, 88425-20-1; **4a**, 88425-21-2; **4b**, 88425-22-3; **4c**, 88425-23-4; **4d**, 88494-18-2; **5a**, 88425-24-5; **6a**, 88425-25-6; **7a**, 88425-26-7; **7b**, 88425-27-8; **7c**, 88425-28-9; **8**, 88425-29-0; **11**, 88425-30-3; (*Z*)-Phe-OH, 1161-13-3; Boc-Phe-OH, 13734-34-4; MeOH, 67-56-1; $PhCH_2OH$, 100-51-6; *N*-acetylphenylalanine, 2018-61-3.

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(2 + 2) Photocycloaddition of the Carbon-Nitrogen Double Bond of Quinoxalin-2(1*H*)-ones to Electron-Deficient Olefins

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The photochemical reactivity of the quinoxalin-2(1*H*)-ones **1a-i** with electron-deficient olefins such as acrylonitrile (**2a**), methacrylonitrile (**2b**), methyl acrylate (**2c**), methyl methacrylate (**2d**), and vinyl acrylate (**2e**) is described. Irradiation of the quinoxalin-2(1*H*)-ones **1a-f,i** in the presence of electron-deficient olefins (**2a-e**) gave the novel regiospecific (2 + 2) cycloadducts (**3-18**) of the carbon-nitrogen double bond of **1** and olefin **2**. The photoreaction of the quinoxalin-2(1*H*)-ones **1** with olefins **2** occurs from a triplet state.

(2 + 2) Photocycloaddition of olefins to carbon-carbon[1,2] and carbon-oxygen double bonds[2,3] has been extensively employed in organic synthesis; however, similar cycloadditions to the carbon-nitrogen double bond are less

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Table I. Yield of (2 + 2) Photocycloadducts 3-18′

product	R^1	R^2	R^3	R^4	yield, % 1:1 cycloadduct	yield, % recovered
3	Me	H	H	CN	29	5
3′	Me	H	CN	H	33	
4	Me	H	CN	Me	91	trace
5	H	H	CN	Me	41	30
6	Me	Me	H	CN	96	trace
7	Me	Me	H	CO_2Me	40	5
8	Me	Me	CN	Me	94	trace
9	Me	Me	Me	CO_2Me	45	trace
9′	Me	Me	CO_2Me	Me	39	
10	Me	Me	H	$CO_2CH=CH_2$	32	trace
11	Et	Me	CN	Me	100	
12	Et	Me	Me	CO_2Me	57	trace
12′	Et	Me	CO_2Me	Me	39	
13	Ph	Me	CN	Me	97	trace
14	Ph	Me	Me	CO_2Me	42	trace
14′	Ph	Me	CO_2Me	Me	39	
15	H	Me	CN	Me	99	trace
16	H	Me	Me	CO_2Me	58	trace
16′	H	Me	CO_2Me	Me	40	
17	H	Me	H	$CO_2CH=CH_2$	50	30
18	H	Ph	Me	CN	10	5
18′	H	Ph	CN	Me	65	

frequently encountered. Intermolecular photocycloadditions[4-7] of olefins to the carbon–nitrogen double bond are known for systems that are conjugated with an imino or a carbonyl group. The first such example involved the photoaddition of 2,5-diphenyl-1,3,4-oxadiazole to indene and furan.[4] Swenton and co-workers reported regioselective photocycloaddition of 6-azauracil and 6-azathymine to a variety of unsaturated linkages.[5] Koch et al. have shown that 3-ethoxyisoindolone and 2-phenyl-2-oxazolin-4-one yielded (2 + 2) photocycloadducts with electron-rich olefins regioselectively.[6] With an electron-deficient olefin such as fumaronitrile, 3-ethoxyisoindolone showed no tendency to undergo (2 + 2) cycloaddition. In search of photochemical reactions of cyclic conjugated nitrogen–carbonyl heterocycles such as pyrimidin-2(1*H*)-ones and pyrazin-2(1*H*)-ones,[8] we have investigated the photocycloaddition of quinoxalin-2(1*H*)-ones to electron-deficient olefins. This paper describes the regioselective photocycloaddition reaction of quinoxalin-2(1*H*)-ones **1a–i**.

Irradiation of a solution of 1-methylquinoxalin-2(1*H*)-one (**1a**) in benzene in the presence of an excess acrylonitrile (**2a**) with a high-pressure mercury lamp through a Pyrex filter under nitrogen at room temperature for 15 h gave two 1:1 cycloadducts in 29% and 33% isolated yields,

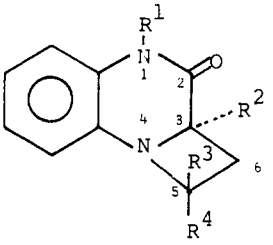

Figure 1.

respectively. The usual analytical and spectroscopic data indicated these photoproducts **3** and **3′** to be 1:1 adducts, and the regiochemistry of the 1:1 adducts **3** and **3′** was suggested by the chemical shifts of the azetidine ring methine and methylene protons[9] of the 1:1 cycloadducts. Thus, the 1:1 cycloadduct **3** showed methine and methylene protons at δ 4.52–4.70 (m, 2 H) and 2.88–3.42 (m, 2 H), and **3′** showed methine and methylene protons at δ 4.57 (dd, 1 H, J = 3.9, 8.8 Hz), 4.80 (dd, 1 H, J = 3.9, 7.8 Hz), and 2.91 (ddd, 1 H, J = 3.9, 7.8, 12.2 Hz), and 3.22–3.52 (m, 1 H). The chemical shifts of methylene protons of the other regioisomer **3″** would be at a lower field due to the electronegativity of the adjacent nitrogen. The stereochemistry of the 1:1 cycloadducts **3** and **3′** was uncertain.[10] When a solution of the quinoxalin-2(1*H*)-one **1a** in benzene was irradiated in the presence of the α-substituted olefin methacrylonitrile (**2b**) under the same conditions, the (2 + 2) photocycloadduct **4** was isolated in 91% yield. The NMR spectrum of this photoproduct indicated that the methylene proton at δ 3.18 (m, 2 H) was coupled with a methine proton at δ 4.46 (dd, 1 H, J = 3.4, 7. 8 Hz) consistent with the regiochemistry assigned to the cycloadduct **4**.

Irradiation of the quinoxalin-2(1*H*)-ones **1b–f** in benzene or methanol–methylene chloride[11] under the same conditions as described above in the presence of acrylonitrile

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(10) The stereochemistry of all 1:1 cycloadducts **3**, **3′**, **4–6**, **8**, **11**, **13**, **15**, **18**, and **18′** was uncertain and was tentatively assigned as shown in Figure 1 by the similarity of the NMR spectra. The chemical shift of the methyl protons at C-5 of **18** (δ 1.55) was observed in higher field than those of another stereoisomers **4**, **5**, **8**, **11**, **13**, **15**, and **18′** (δ 1.75–1.86) due to the anisotropic effect of the benzene ring.
(11) The quinoxalin-2(1*H*)-ones **1b**,**f**,**i** were insoluble in benzene.

Table II. Photoreactions of the Quinoxalin-2(1*H*)-one 1c[a] in the Presence of Electron-Deficient Olefins 2b,d under Various Conditions

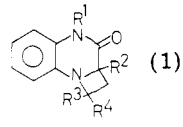
run	olefin	solv	irradiatn time, h	conditns	yield of 1:1 cycloadducts,[f] % 8	9	9′	recovered 1c
1	2b	benzene	3	N_2, >300 nm	88			~0
2	2b	benzene	15	N_2, >300 nm	94			~0
3	2b	MeOH	15	N_2, >300 nm	72			~0
4	2b	CH_3CN	15	N_2, >300 nm	58			~0
5	2b	acetone	15	N_2, >300 nm	97			~0
6	2b	benzene	3	O_2,[b] >300 nm	29			55
7	2b	benzene	3	N_2, >300 nm *m*-methoxyacetophenone[c]	90			ND[g]
8	2b	benzene	3	N_2, 366 nm[d]	90			~0
9	2b	benzene	3	N_2, 366 nm[d] *trans*-stilbene[e]	ND[g]			83
10	2d	benzene	3	N_2, >300 nm		44	38	~0
11	2d	benzene	15	N_2, >300 nm		45	39	~0
12	2d	acetone	15	N_2, >300 nm		44	32	~0
13	2d	benzene	3	O_2,[b] >300 nm		8	<1	70
14	2d	benzene	15	O_2,[b] >300 nm		12	2	52
15	2d	benzene	3	N_2, >300 nm *m*-methoxyacetophenone[c]		38	50	ND[g]
16	2d	benzene	3	N_2, 366 nm[d]		44	41	~0
17	2d	benzene	3	N_2, 366 nm[d] *trans*-stilbene[e]		ND[g]	ND[g]	85

[a] UV spectrum of 1,3-dimethylquinoxalin-2(1*H*)-one (**1c**): λ_{max} (EtOH) 210 (ϵ 17 200), 230 (22 200), 279 (5600), 329 (sh, 6400), and 338 nm (6500). **1c** showed an end absorption until 380 nm (ϵ 960 at 366 nm). [b] Oxygen was bubbling. [c] *m*-Methoxyacetophenone absorbed more than 95% light. [d] A Pyrex glass filter and a methanol solution of naphthalene (5 g/1 L) were used to isolate the 366-nm region. [e] UV spectrum of *trans*-stilbene shows no absorption at 366 nm, and 10 molar equiv *trans*-stilbene was used. [f] Isolated yield. [g] Not detected.

(**2a**) or methacrylonitrile (**2b**) gave one stereoisomer of 1:1 cycloadducts **5**, **6**, **8**, **11**, **13**, and **15** in 41–100% isolated yields. In the case of 1-phenyl-3-methylquinoxalin-2-

1a, R^1 = Me, R^2 = H
b, R^1 = H, R^2 = H
c, R^1 = Me, R^2 = Me
d, R^1 = Et, R^2 = Me
e, R^1 = Ph, R^2 = Me
f, R^1 = H, R^2 = Me
g, R^1 = Me, R^2 = Ph
h, R^1 = Et, R^2 = Ph
i, R^1 = H, R^2 = Ph

2a, R^3 = H, R^4 = CN
b, R^3 = Me, R^4 = CN
c, R^3 = H, R^4 = CO_2Me
d, R^3 = Me, R^4 = CO_2Me
e, R^3 = H, R^4 = $CO_2CH{=}CH_2$



(1)

3–18′

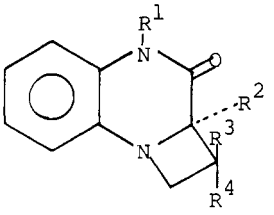
(1*H*)-one (**1i**), two stereisomers of the 1:1 cycloadducts **18** and **18′** were obtained (Table I). The structure of these 1:1 cycloadducts was established by their spectroscopic properties and elemental analyses (Experimental Section). Characteristically these 1:1 cycloadducts showed a carbonyl stretching band at 1680–1650 cm^{-1} and no carbon–nitrogen double-bond stretching band in the infrared spectrum. Irradiation of the quinoxalin-2(1*H*)-ones **1c–f** in the presence of methyl acrylate (**2c**) or methyl methacrylate (**2d**) under the same conditions also yielded the 1:1 cycloadducts **7**, **9**, **9′**, **12**, **12′**, **14**, **14′**, **16**, and **16′** in 32–57% yields. Use of methyl methacrylate (**2d**) inevitably gave two stereoisomeric 1:1 cycloadducts. The assignment of the regiochemistry was based upon the chemical shifts and splitting patterns of the azetidine ring methine and methylene protons of the 1:1 cycloadducts in the NMR spectra. One methine proton of the cycloadduct **7** appeared as a doublet of doublets at δ 4.33 (J = 7.8, 9.3 Hz) and two methylene protons appeared as two doublets of doublets at δ 3.13 (J = 9.3, 11.7 Hz) and 2.63 (J = 7.8, 11.7 Hz), respectively. The stereochemistry was tentatively assigned as shown in Figure 1 on the basis of the NMR spectrum (Experimental Section). The C-5 methyl protons (δ 1.32–1.49) of the 1:1 cycloadducts **9**, **12**, **14**, and **16** appeared as a singlet in higher field than those (δ 1.74–1.78) of the stereoisomers **9′**, **12′**, **14′**, and **16′** due to the anisotropic effect of the benzene ring. On the other hand, the methoxycarbonyl methyl protons of **9**, **12**, **14**, and **16** were observed at a lower field than those of **9′**, **12′**, **14′**, and **16′**. Additional evidence for the stereochemical assignment appears in the ^{13}C NMR spectra. The C-5 methyl carbon signal of the cycloadducts **9**, **12**, **14**, and **16** (20.4–20.8 ppm) appeared upfield from the corresponding signal of the stereoisomers **9′**, **12′**, **14′**, and **16′** (27.9–28.3 ppm) by ~7.5 ppm.

When the quinoxalin-2(1*H*)-ones **1c,f** were irradiated in the presence of vinyl acrylate (**2e**) under the same conditions for 6 h,[12] the 1:1 cycloadducts **10** and **17** were obtained in 32% and 50% isolated yields, respectively. The structure of the 1:1 adducts **10** and **17** was confirmed with use of spectral data and elemental analyses. On the other hand, irradiation of 1-methyl- and 1-ethyl-3-phenylquinoxalin-2(1*H*)-ones (**1g** and **1h**) in benzene in the presence of methacrylonitrile (**2b**) or methyl methacrylate (**2d**) under the same conditions gave no 1:1 cycloadducts and the quinoxalin-2(1*H*)-ones 1g,h were recovered quantitatively. Irradiation of 1,3-dimethylquinoxalin-2(1*H*)-one (**1c**) in the presence of β-substituted electron-deficient olefins such as methyl crotonate, methyl β-ethoxyacrylate, dimethyl fumarate, maleic anhydride, crotononitrile, and fumaronitrile gave small amounts of several unseparable mixtures, and 1:1 cycloadducts could not be isolated.

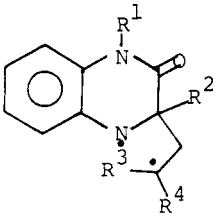
Irradiation of 1,3-dimethylquinoxalin-2(1*H*)-one (**1c**) in the presence of methacrylonitrile (**2b**) or methyl methacrylate (**2d**) under various conditions was carried out (Table II). The yields of the 1:1 cycloadducts **8**, **9**, and **9′** decreased under an oxygen atmosphere (runs 6, 13, and

(12) Longer irradiation resulted in polymerization.

14). Furthermore, the formation of the 1:1 cycloadducts **8**, **9**, and **9′** was completely quenched by *trans*-stilbene as a triplet quencher (runs 9 and 17). The isolated amount of the 1:1 cycloadducts **8**, **9**, and **9′** was constant within experimental error when the quinoxalin-2(1*H*)-one **1c** and the electron-deficient olefins **2b** and **2d** were irradiated in the presence of a triplet sensitizer such as *m*-methoxyacetophenone and acetone (runs 5, 7, 12, and 15). These results suggest that the photocycloaddition may occur from the excited triplet state of the quinoxalin-2(1*H*)-one **1c**. The regiochemistry of the photoproduct and the nonstereospecificity of the cycloaddition suggest that the formation of 1:1 cycloadducts may arise by initial interaction of the quinoxalin-2(1*H*)-one triplet with the electron-deficient olefin **2** to give an excited complex or exciplex,[13] which proceeds to give 1,4-biradical intermediate **19**. The



3′′



19

latter cyclizes to give the 1:1 cycloadduct. Similar, 1,4-biradical intermediates have been proposed for both the photoreactions of α,β-unsaturated ketones with olefins and the triplet state Paterno–Büchi reactions.[1,3] It is interesting to note that the photoreaction of the quinoxalin-2(1*H*)-ones **1** with electron-deficient olefins **2** is regiospecific, giving 1:1 cycloadducts **3–18** and that additional conjugation with a carbonyl group is important for (2 + 2) photocycloaddition of electron-deficient olefins to carbon–nitrogen double bonds.

Experimental Section

Melting and boiling points are uncorrected. Melting points were measured with a Yanaco micro melting point apparatus (MP-J3), and boiling points were measured with Büchi Kugel rohr (KR-3) apparatus. Infrared spectra were recorded with a Hitachi 260-30 spectrometer. ^1H and ^{13}C NMR spectra were obtained with a JEOL FX 100 spectrometer. A HALōs (Eikosha EHP-300 W) high-pressure mercury lamp was used as an irradiation source.

Materials. Quinoxalin-2(1*H*)-ones **1a–c,f** were prepared as described in the literature,[14,15] and **1d,e,g–i** were prepared by a modification of these methods.

1-Methylquinoxalin-2(1*H*)-one (1a): mp 120–121 °C (lit.[14] 120–121 °C); UV (EtOH) 206 (ϵ 1.61 × 10^4), 230 (2.34 × 10^4), 280 (5.0 × 10^3), 343.5 nm (5.1 × 10^3); IR (KBr) 1660, 1600, 1590, 1465, 950, 925, 750, 690 cm^{-1}; ^1H NMR δ ($CDCl_3$) 3.69 (s, 3 H), 7.27–7.44 (m, 2 H), 7.52–7.70 (m, 1 H), 7.82–7.90 (m, 1 H), 8.29 (s, 1 H); ^{13}C NMR δ ($CDCl_3$) 28.7 (q), 113.7 (d), 123.6 (d), 130.3 (d), 130.9 (d), 133.1 (2 × s), 150.1 (d), 154.9 (s).

Quinoxalin-2(1*H*)-one (1b): mp 266–267 °C (lit.[15] 267–269 °C); IR (KBr) 3150, 1695, 1685, 1635, 895, 780, 760, 750, 723 cm^{-1}; ^1H NMR δ (Me_2SO-d_6) 7.29–7.93 (m, 4 H), 8.27 (s, 1 H), 12.51 (br s, 1 H); ^{13}C NMR δ (Me_2SO-d_6) 115.8 (d), 123.2 (d), 128.8 (d), 130.7 (d), 131.9 (s), 132.1 (s), 151.6 (d), 154.9 (s).

1,3-Dimethylquinoxalin-2(1*H*)-one (1c): mp 83–84 °C (lit.[14] 85–86 °C); UV (EtOH) 210 ϵ (1.72 × 10^4), 230 (2.22 × 10^4) 279 (5.6 × 10^3), 329 (sh, 6.4 × 10^3), 338 nm (6.5 × 10^3); IR (KBr) 1645, 1595, 1470, 760, 735 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.58 (s, 3 H), 3.68 (s, 3 H), 7.22–7.61 (m, 3 H), 7.73–7.83 (m, 1 H); ^{13}C NMR δ ($CDCl_3$) 21.5 (q), 28.9 (q), 113.5 (d), 123.5 (d), 129.3 (d), 129.4 (d), 132.5 (s), 133.1 (s), 155.1 (s), 158.2 (s).

1-Ethyl-3-methylquinoxalin-2(1*H*)-one (1d): mp 93–94 °C; UV (EtOH) 209 (ϵ 8.2 × 10^3), 230 (9.2 × 10^3), 279 (2.3 × 10^3), 327 (sh, 2.5 × 10^3), 338 nm (2.7 × 10^3); IR (KBr) 1645, 1600, 1460, 780, 765, 755 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.37 (t, 3 H), 2.59 (s, 3 H), 4.31 (q, 2 H), 7.22–7.61 (m, 3 H), 7.76–7.86 (m, 1 H); ^{13}C NMR δ ($CDCl_3$) 12.3 (q), 21.4 (q), 37.2 (t), 113.2 (d), 123.2 (d), 129.4 (d), 129.5 (d), 132.0 (s), 132.8 (s), 154.5 (s), 158.2 (s). Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.42; N, 14.88. Found: C, 70.10; H, 6.42; N, 14.90.

1-Phenyl-3-methylquinoxalin-2(1*H*)-one (1e): mp 198–199 °C; UV (EtOH) 210 (ϵ 2.29 × 10^4), 230 (1.99 × 10^4), 279 (5.4 × 10^3), 335 nm (5.5 × 10^3); IR (KBr) 1650, 1598, 1460, 750, 695 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.63 (s, 3 H), 6.56–6.74 (m, 1 H), 7.20–7.38 (m, 4 H), 7.46–7.63 (m, 3 H), 7.70–7.88 (m, 1 H); ^{13}C NMR δ ($CDCl_3$) 21.4 (q), 115.4 (d), 123.6 (d), 128.2 (2 × d), 129.0 (d), 129.3 (d), 130.2 (2 × d), 132.5 (s), 134.0 (s), 135.8 (s), 154.8 (s), 159.0 (s). Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25: H, 5.11; N, 11.85. Found: C, 75.95; H, 5.09; N, 11.79.

3-Methylquinoxalin-2(1*H*)-one (1f): mp 241–242 °C (lit.[16] 245 °C); IR (KBr) 3175, 3100, 2850, 1660, 890, 755 cm^{-1}; ^1H NMR δ (Me_2SO-d_6) 2.51 (s, 3 H), 7.26–7.84 (m, 4 H), 12.40 (br s, 1 H); ^{13}C NMR δ (Me_2SO-d_6) 20.6 (q), 115.3 (d), 123.0 (d), 127.9 (d), 129.3 (d), 131.7 (s), 132.0 (s), 155.0 (s), 159.2 (s).

1-Methyl-3-phenylquinoxalin-2(1*H*)-one (1g): mp 135–136 °C; UV (EtOH) 213 (ϵ 2.62 × 10^4), 224 (2.49 × 10^4), 304 (1.15 × 10^4), 359 nm (1.18 × 10^4); IR (KBr) 1640, 1595, 1465, 760, 745, 735, 690 cm^{-1}; ^1H NMR δ ($CDCl_3$) 3.71 (s, 3 H), 7.21–7.61 (m, 6 H), 7.85–7.96 (m, 1 H), 8.20–8.34 (m, 2 H). Anal. Calcd for $C_{15}H_{12}N_2O$: C, 76.25: H, 5.11: N, 11.85. Found: C, 76.15; H, 4.98; N, 11.82.

1-Ethyl-3-phenylquinoxalin-2(1*H*)-one (1h): mp 97–98 °C; UV (EtOH) 210 (ϵ 2.82 × 10^4), 225 (2.57 × 10^4), 303 (1.16 × 10^4), 359 nm (1.20 × 10^4); IR (KBr) 1640, 1600, 1465, 765, 758, 740, 698 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.41 (t, 3 H), 4.37 (q, 2 H), 7.25–7.60 (m, 6 H), 7.89–8.00 (m, 1 H), 8.25–8.37 (m, 2 H). Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.77; H, 5.63; N, 11.19. Found: C, 76.62; H, 5.63; N, 11.16.

3-Phenylquinoxalin-2(1*H*)-one (1i): mp 250–251 °C; IR (KBr) 3100, 2880, 2830, 1660, 905, 760, 685 cm^{-1}; ^1H NMR δ (Me_2SO-d_6) 7.33–7.74 (m, 6 H), 7.90–8.00 (m, 1 H), 8.33–8.48 (m, 2 H), 12.69 (br s, 1 H). Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.53; N, 12.60. Found: C, 75.37; H, 4.52: N, 12.66.

General Procedure for the Photochemical Reactions of the Quinoxalin-2(1*H*)-ones 1a–i. A solution of 200 mg of the quinoxalin-2(1*H*)-one **1** in 50 mL of benzene (for **1a,c–e,g,h**) or methanol–methylene chloride (2:1) (for **1b,f,i**) in the presence of a large excess of electron-deficient olefin **2** (ca. 1 mL) was irradiated under nitrogen with a high-pressure mercury lamp through a Pyrex filter for 3–15 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel column with benzene–ethyl acetate (4:1–19:1) or methylene chloride–ethyl acetate (4:1–9:1) as eluent to give the corresponding (2 + 2) photocycloadducts **3–18**.

Photocycloadduct 3: mp 142–143 °C; IR (KBr) 2230, 1655, 1598, 1503, 1385, 745 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.88–3.42 (m, 2 H), 3.39 (s, 3 H), 4.52–4.70 (m, 2 H), 6.90–7.21 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 28.6 (q), 30.4 (t), 53.8 (d), 57.7 (d), 115.0 (d), 118.7 (s), 122.2 (d), 124.1 (d), 125.8 (d), 132.5 (s), 133.2 (s), 166.7 (s). Anal.

(13) The spectroscopic evidence for the formation of an excited complex could not be obtained.
(14) Cheeseman, G. W. H. *J. Chem. Soc.* **1955**, 1804.
(15) Cheeseman, G. W. H. *J. Chem. Soc.* **1957**, 3236.
(16) Kröhnke, F. *Chem. Ber.* **1947**, 298.

Calcd for $C_{12}H_{11}N_3O$: C, 67.59: H, 5.19: N, 19.70. Found: C, 67.20: H, 5.18: N, 19.50.

Photocycloadduct 3′: mp 185–186 °C; IR (KBr) 2240, 1650, 1602, 1500, 1375, 778, 758 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.91 (ddd, 1 H, J = 3.9, 7.8, 12.2 Hz), 3.22–3.52 (m, 1 H), 3.42 (s, 3 H), 4.57 (dd, 1 H, J = 3.9, 8.8 Hz), 4.80 (dd, 1 H, J = 3.9, 7.8 Hz), 6.79–7.18 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 28.7 (q), 29.9 (t), 54.1 (d), 58.9 (d), 115.3 (d), 116.8 (s), 122.4 (d), 123.9 (d), 125.8 (d), 130.2 (s), 134.6 (s), 166.2 (s). Anal. Calcd for $C_{12}H_{11}N_3O$: C, 67.59: H, 5.19: N, 19.70. Found: C, 67.25; H, 5.25; N, 19.78.

Photocycloadduct 4: mp 99.5–100 °C; IR (KBr) 2225, 1665, 1598, 1502. 1370, 760, 740 cm^{-1}; ^1H NMR δ ($CCCl_3$) 1.78 (s, 3 H), 2.83–3.18 (m, 2 H), 3.41 (s, 3 H), 4.46 (dd, 1 H, J = 3.4, 7.8 Hz), 6.81–7.27 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 27.8 (q), 28.6 (q), 37.6 (t), 55.7 (d), 63.5 (s), 115.4 (d), 119.1 (s), 122.9 (d), 123.7 (d), 126.2 (d), 130.1 (s), 134.9 (s), 166.7 (s). Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70: H, 5.76; N, 18.48. Found: C, 68.52: H, 5.72; N, 18.54.

Photocycloadduct 5: mp 234 °C dec; IR (KBr) 3180, 3130, 2225, 1675, 1600, 1495, 1400, 763 cm^{-1}; ^1H NMR δ (Me_2SO-d_6) 1.86 (s, 3 H), 2.96 (dd, 1 H, J = 4.4, 12.2 Hz), 3.11 (dd, 1 H, J = 8.3, 12.2 Hz), 4.57 (dd, 1 H, J = 4.4, 8.3 Hz), 6.97–7.30 (m, 4 H), 10.70 (br s, 1 H); ^{13}C NMR δ (Me_2SO-d_6) 27.3 (q), 36.3 (t), 55.2 (d), 63.7 (s), 116.1 (d), 119.9 (s), 122.3 (d), 123.1 (d), 125.6 (d), 129.1 (s), 133.0 (s), 166.7 (s). Anal. Calcd for $C_{12}H_{11}N_3O$: C, 67.59; H, 5.19; N, 19.70. Found: C, 67.32; H, 5.21; N, 19.64.

Photocycloadduct 6: mp 138.5–140 °C; IR (KBr) 2220, 1655, 1597, 1498, 1365, 765, 745, 695 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.51 (s, 3 H), 2.89 (dd, 1 H, J = 7.8, 11.7 Hz), 3.10 (dd, 1 H, J = 3.4, 11.7 Hz), 3.43 (s, 3 H), 4.66 (dd, 1 H, J = 3.4, 7.8 Hz), 6.86–7.21 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 26.1 (q), 29.2 (q), 36.4 (t), 50.8 (d), 65.2 (s), 115.4 (d), 117.0 (s), 123.5 (d), 123.8 (d), 126.0 (d), 129.2 (s), 135.1 (s), 168.9 (s). Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.67; N, 18.48. Found: C, 68.40; H, 5.78; N, 18.41.

Photocycloadduct 7: bp 140 °C (2 mmHg); IR (film) 1740, 1655, 1598, 1502, 1378, 1215, 1115, 1050, 755, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.53 (s, 3 H), 2.63 (dd, 1 H, J = 7.8, 11.7 Hz), 3.13 (dd, 1 H, J = 9.3, 11.7 Hz), 3.39 (s, 3 H), 3.82 (s, 3 H), 4.33 (dd, 1 H, J = 7.8, 9.3 Hz), 6.88–7.21 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 26.5 (q), 28.8 (q), 35.9 (t), 52.0 (q), 62.0 (s), 62.0 (d), 114.5 (d), 123.0 (d), 123.5 (d), 124.4 (d), 132.7 (s), 133.0 (s), 169.5 (s). 172.1 (s). Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.19; N, 10.76. Found: C, 64.36; H, 6.28; N, 10.65.

Photocycloadduct 8: bp 130 °C (2 mmHg); mp 100–100.5 °C; IR (KBr) 2220, 1660, 1595, 1500, 1370, 760, 750 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.48 (s, 3 H), 1.75 (s, 3 H), 2.50 (d, 1 H, J = 12.0 Hz), 3.24 (d, 1 H, J = 12.0 Hz), 3.39 (s, 3 H), 6.85–7.28 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 26.3 (q), 27.8 (q), 28.8 (q), 44.0 (t), 59.5 (s), 61.5 (s), 115.3 (d), 119.0 (s), 123.5 (d), 123.6 (d), 126.1 (d), 128.8 (s), 134.9 (s), 168.9 (s). Anal. Calcd for $C_{14}H_{15}N_3O$: C, 69.68; H, 6.26; N, 17.41. Found: C, 69.64; H, 6.30; N, 17.54.

Photocycloadduct 9: bp 145 °C (2 mmHg), mp 112.5–113 °C; IR (KBr) 1730, 1660, 1595, 1495, 1375, 1290, 1165, 1103, 745, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.32 (s, 3 H), 1.51 (s, 3 H), 2.79 (d, 1 H, J = 12.2 Hz), 2.94 (d, 1 H, J = 12.2 Hz), 3.40 (s, 3 H), 3.83 (s, 3 H), 6.86–7.23 (m, 4 H); ^1C NMR δ ($CDCl_3$) 20.5 (q), 26.8 (q), 28.9 (q), 42.3 (t), 52.3 (q), 59.9 (s), 66.3 (s), 114.6 (d), 123.3 (d), 123.4 (d), 123.7 (d), 129.6 (s), 134.0 (s), 167.0 (s), 174.5 (s). Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61; N, 10.21. Found: C, 65.42; H, 6.59; N, 10.13.

Photocycloadduct 9′: bp 140 °C (2 mmHg); IR (film) 1745, 1665, 1595, 1500, 1370, 1300, 1160, 1105, 745, 695 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.52 (s, 3 H), 1.74 (s, 3 H), 2.31 (d, 1 H, J = 12.2 Hz), 3.30 (d, 1 H, J = 12.2 Hz), 3.36 (s, 3 H), 3.37 (s, 3 H), 6.68–7.13 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 26.7 (q), 28.1 (q), 28.9 (q), 42.2 (t), 51.5 (q), 60.6 (s), 69.2 (s), 114.6 (d), 120.7 (d), 123.0 (d), 123.2 (d), 131.3 (s), 133.6 (s), 168.9 (s), 172.1 (s). Anal. Calcd for $C_{15}H_{18}N_2O_3$: C, 65.67; H, 6.61; N, 10.21. Found: C, 65.57; H, 6.66; N, 10.06.

Photocycloadduct 10: bp 140 °C (2 mmHg); IR (film) 1760, 1665, 1597, 1500, 1375, 1175, 750 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.54 (s, 3 H), 2.66 (dd, 1 H, J = 7.8, 11.7 Hz), 3.17 (dd, 1 H, J = 9.3, 11.7 Hz), 3.40 (s, 3 H), 4.40 (dd, 1 H, J = 7.8, 9.3 H), 4.69 (dd, 1 H, J = 2.0, 6.4 Hz), 4.99 (dd, 1 H, J = 2.0, 13.7 Hz), 6.76–7.19 (m, 4 H), 7.36 (dd, 1 H, J = 6.4, 13.7 Hz); ^{13}C NMR δ ($CDCl_3$) 26.5 (q), 28.9 (q), 35.8 (t), 61.8 (d), 62.2 (s), 98.6 (t), 114.6 (d), 123.4 (d), 123.6 (d), 124.7 (d), 132.6 (s), 133.3 (s), 140.8 (d), 168.9 (s), 169.5 (s). Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5..92; N, 10.28. Found: C, 65.87; H, 5.94; N, 10.31.

Photocycloadduct 11: mp 119.5–121 °C; IR (KBr) 2210, 1660, 1595, 1497, 1383, 760 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.27 (t, 3 H), 1.47 (s, 3 H), 1.75 (s, 3 H), 2.50 (d, 1 H, J = 11.7 Hz), 3.23 (d, 1 H, J = 11.7 Hz), 3.85–4.28 (m, 2 H), 6.86–7.22 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 11.9 (q), 26.5 (q), 28.1 (q), 36.7 (t), 44.2 (t), 59.7 (s), 61.5 (s), 115.4 (d), 119.4 (s), 123.5 (d), 124.3 (d), 126.3 (d), 129.3 (s), 133.7 (s), 168.6 (s). Anal. Calcd for $C_{15}H_{17}N_2O$: C, 70.56; H, 6.71; N, 16.45. Found: C, 70.44; H, 6.67; N, 16.45.

Photocycloadduct 12: bp 138 °C (2 mmHg); IR (film) 1735, 1665, 1595, 1495, 1390, 1165, 750, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.23 (t, 3 H), 1.32 (s, 3 H), 1.49 (s, 3 H), 2.78 (d, 1 H, J = 11.7 Hz), 2.92 (d, 1 H, J = 11.7 Hz), 3.83 (s, 3 H), 4.03 (q, 2 H), 6.76–7.25 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 12.1 (q), 20.4 (q), 26.4 (q), 36.2 (t), 42.0 (t), 52.1 (q), 59.5 (s), 66.2 (s), 114.4 (d), 123.1 (d), 123.7 (2 × d) 129.8 (s) 132.5 (s), 169.3 (s), 174.4 (s). Anal. Calcd for $C_{16}H_{20}N_2O$: C, 66.64; H, 6.99; N, 9.71. Found: C, 66.40: H, 7.08; N, 9.63.

Photocycloadduct 12′: bp 145 °C (2 mmHg); IR (film) 1735, 1660, 1595, 1497, 1385, 1160, 740 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.25 (t, 3 H), 1.51 (s, 3 H), 1.74 (s, 3 H), 2.29 (d, 1 H, J = 11.7 Hz), 3.31 (d, 1 H, J = 11.7 Hz), 3.37 (s, 3 H), 4.01 (q, 2 H), 6.68–7.02 (m, 4 H); ^{13}C NMR δ ($CDCl_3$) 12.2 (q), 26.8 (q), 28.0 (q), 36.3 (t), 42.1 (t), 51.5 (q), 60.6 (s), 69.0 (s), 114.4 (d), 120.9 (d), 122.8 (d), 123.1 (d), 131.4 (s), 131.8 (s), 167.9 (s), 172.3 (s). Anal. Calcd for $C_{16}H_{20}N_2O_3$: C, 66.64; H, 6.99; N, 9.71. Found: C, 66.48: H, 7.01; N, 9.74.

Photocycloadduct 13: mp 168.5–169.5 °C; IR (KBr) 2220, 1675, 1595, 1495, 1370, 1360, 1300, 760, 720, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.62 (s, 3 H), 1.79 (s, 3 H), 2.55 (d, 1 H, J = 11.7 Hz), 3.32 (d, 1 H, J = 11.7 Hz), 6.27–6.42 (m, 1 H), 6.90–7.06 (m, 3 H), 7.22–7.60 (m, 5 H); ^{13}C NMR δ ($CDCl_3$) 26.5 (q), 27.9 (q), 44.3 (t), 60.2 (s), 62.6 (s), 117.7 (d), 119.7 (s), 123.9 (d), 124.2 (d), 126.2 (d), 128.6 (s), 136.7 (s), 137.4 (s), 169.3 (s). Anal. Calcd for $C_{19}H_{17}N_3O$: C, 75.22; H, 5.64; N, 13.85. Found: C, 75.01; H, 5.63; N, 13.82.

Photocycloadduct 14: mp 108.5–109 °C; IR (Kbr) 1720, 1680, 1595, 1495, 1370, 1360, 1295, 1165, 760, 705 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.49 (s, 3 H), 1.64 (s, 3 H), 2.84 (d, 1 H, J = 12.2 Hz), 2.98 (d, 1 H, J = 12.2 Hz), 3.83 (s, 3 H), 6.23 (dd, 1 H, J = 1.5, 7.8 Hz), 6.71–7.03 (m, 2 H), 7.20–7.62 (m, 6 H); ^{13}C NMR δ ($CDCl_3$) 20.5 (q), 26.5 (q), 41.9 (t), 52.1 (q), 60.4 (s), 66.4 (s), 116.5 (d), 123.4 (2 × d), 128.0 (d), 128.7 (d), 129.0 (s), 129.7 (2 × d), 135.3 (s), 137.3 (s), 169.8 (s), 174.3 (s). Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.32. Found: C, 71.39: H, 5.93; N, 8.35.

Photocycloadduct 14′: bp 165 °C (2 mmHg); IR (film) 1725, 1680, 1590, 1495, 1365, 1355, 1150, 745, 700 cm^{-1}; ^1H NMR δ ($CCCl_3$) 1.64 (s, 3 H), 1.78 (s, 3 H), 2.34 (d, 1 H, J = 11.7 Hz), 3.34 (d, 1 H, J = 11.7 H), 3.49 (s, 3 H), 6.16–6.29 (m, 1 H), 6.63–6.95 (m, 3 H), 7.21–7.60 (m, 5 H); ^{13}C NMR δ ($CDCl_3$) 26.7 (q), 27.9 (q), 42.2 (t), 51.8 (q), 61.1 (s), 69.3 (s), 116.5 (d), 120.7 (d), 122.8 (d), 128.0 (2 × d), 128.9 (d), 129.6 (2 × d), 130.8 (s), 134.9 (s), 137.9 (s), 168.7 (s), 172.3 (s). Anal. Calcd for $C_{20}H_{20}N_2O_3$: C, 71.41; H, 5.99; N, 8.32. Found: C, 71.31; H, 6.02; N, 8.26.

Photocycloadduct 15: mp 183–184 °C; IR (KBr) 3200, 3140, 2225, 1680, 1500, 1385, 765, 685 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.58 (s, 3 H), 1.79 (s, 3 H), 2.53 (d, 1 H, J = 12.2 Hz), 3.34 (d, 1 H, J = 12.2 Hz), 6.83–7.21 (m, 4 H), 9.21 (br s, 1 H); ^{13}C NMR δ ($CDCl_3$) 27.0 (q), 28.5 (q), 43.7 (t), 60.1 (s), 62.1 (s), 116.5 (d), 119.4 (s), 123.2 (d), 124.2 (d), 126.3 (d), 128.1 (s), 132.2 (s), 170.6 (s). Anal. Calcd for $C_{13}H_{13}N_3O$: C, 68.70; H, 5.67; N, 18.14. Found: C, 68.58; H, 5.77; N, 18.44.

Photocycloadduct 16: mp 144.5–145.5 °C; IR (KBr) 3200, 3135, 1740, 1670, 1600, 1500, 1390, 1305, 1100, 760, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.37 (s, 3 H), 1.59 (s, 3 H), 2.82 (d, 1 H, J = 12.2 Hz), 2.97 (d, 1 H, J = 12.2 Hz), 3.85 (s, 3 H), 6.78–7.19 (m, 4 H), 9.83 (br s, 1 H); ^{13}C NMR δ ($CDCl_3$) 20.8 (q), 26.9 (q), 42.0 (t), 52.4 (q), 60.4 (s), 66.7 (s), 115.7 (d), 123.1 (d), 123.9 (2 × d), 129.6 (s), 131.4 (s), 172.1 (s), 174.7 (s). Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.19; N, 10.76. Found: C, 64.55; H, 6.16; N, 10.74.

Photocycloadduct 16′: mp 144–146 °C; IR (KBr) 3200, 3130, 1745, 1680, 1597, 1497, 1380, 1310, 1165, 1155, 755, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.61 (s, 3 H), 1.75 (s, 3 H), 2.32 (d, 1 H, J = 12.2 Hz), 3.37 (d, 1 H, J = 12.2 Hz), 3.38 (s, 3 H), 6.66–6.94 (m, 4 H), 9.52 (br s, 1 H); ^{13}C NMR δ ($CDCl_3$) 26.7 (q), 28.3 (q), 41.7 (t), 51.9 (q), 61.2 (s), 69.6 (s), 115.8 (d), 120.5 (d), 123.5 (2 × d), 130.3

(s), 130.9 (s), 170.8 (s), 172.3 (s). Anal. Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.19; N, 10.76. Found: C, 64.38; H, 6.17; N, 10.67.

Photocycloadduct 17: mp 141-142 °C; IR (KBr) 3200, 3130, 1775, 1670, 1650, 1595, 1495, 1380, 1200, 1130, 760 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.63 (s, 3 H), 2.70 (dd, 1 H, J = 7.8, 11.7 Hz), 3.23 (dd, 1 H, J = 8.8, 11.7 Hz), 4.45 (dd, 1 H, J = 7.8, 8.8 Hz), 4.70 (dd, 1 H, J = 2.0, 6.4 Hz), 5.00 (dd, 1 H, J = 2.0, 14.3 Hz), 6.80-7.19 (m, 4 H), 7.37 (dd, 1 H, J = 6.4, 14.3 Hz), 9.99 (br s, 1 H); ^{13}C NMR δ ($CDCl_3$) 26.6 (q), 35.3 (t), 62.1 (d), 62.8 (s), 98.8 (t), 115.8 (d), 123.0 (d), 124.2 (d), 124.9 (d), 130.6 (s), 131.7 (s), 140.9 (d), 169.0 (s), 171.2 (s). Anal. Calcd for $C_{14}H_{14}N_2O_3$: C, 65.10; H, 5.64; N, 10.84. Found: C, 64.92; H, 5.48; N, 10.67.

Photocycloadduct 18: mp 191-192 °C; IR (KBr) 3185, 2150, 1675, 1600, 1495, 1370, 770, 745, 700 cm^{-1}; ^1H NMR δ ($CDCl_3$-Me_2SO-d_6) 1.55 (s, 3 H), 3.20 (d, 1 H, J = 5.4 Hz), 3.30 (d, 1 H, J = 5.4 Hz), 6.82-7.06 (m, 4 H), 7.28-7.52 (m, 5 H), 10.63 (br s, 1 H); ^{13}C NMR δ ($CDCl_3$-Me_2SO-d_6) 20.0 (q), 42.4 (t), 54.9 (s), 63.5 (s), 114.3 (d), 119.8 (s), 120.2 (d), 121.6 (d), 122.9 (2 × d), 123.4 (d), 126.0 (d), 126.6 (2 × d), 131.0 (2 × s), 139.6 (s), 165.2 (s). Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.22; N, 14.52. Found: C, 74.84; H, 5.23; N, 14.32.

Photocycloadduct 18′: mp 250 °C (sublimation); IR (KBr) 3270, 2225, 1680, 1650, 1600, 1505, 1490, 1355, 765, 695 cm^{-1}; ^1H NMR δ ($CDCl_3$-Me_2SO-d_6) 1.79 (s, 3 H), 2.27 (d, 1 H, J = 11.7 Hz), 3.52 (d, 1 H, J = 11.7 Hz), 6.88-7.13 (m, 4 H), 7.25-7.49 (m, 5 H), 10.69 (br s, 1 H); ^{13}C NMR δ ($CDCl_3$-Me_2SO-d_6) 26.0 (q), 42.7 (t), 58.1 (s), 63.5 (s), 114.6 (d), 117.9 (s), 121.2 (d), 121.6 (d), 123.2 (2 × d), 124.3 (d), 126.1 (d), 126.6 (2 × d), 131.6 (s), 131.7 (s), 139.6 (s), 165.0 (s). Anal. Calcd for $C_{18}H_{15}N_3O$: C, 74.72; H, 5.22; N, 14.52. Found: C, 74.93; H, 5.21; N, 14.47.

Registry No. **1a**, 6479-18-1; **1b**, 1196-57-2; **1c**, 3149-25-5; **1d**, 73148-14-8; **1e**, 21943-45-3; **1f**, 14003-34-0; **1g**, 2048-37-5; **1h**, 88392-55-6; **1i**, 1504-78-5; **2a**, 107-13-1; **2b**, 126-98-7; **2c**, 96-33-3; **2d**, 80-62-6; **2e**, 2177-18-6; **3**, 88392-56-7; **3′**, 88392-57-8; **4**, 88392-58-9; **5**, 88392-59-0; **6**, 88392-60-3; **7**, 88392-61-4; **8**, 88392-62-5; **9**, 88392-63-6; **9′**, 88392-64-7; **10**, 88392-65-8; **11**, 88392-66-9; **12**, 88392-67-0; **12′**, 88392-68-1; **13**, 88392-69-2; **14**, 88392-70-5; **14′**, 88392-71-6; **15**, 88392-72-7; **16**, 88392-73-8; **16′**, 88392-74-9; **17**, 88392-75-0; **18**, 88392-76-1; **18′**, 88392-77-2; O_2, 7782-44-7; *m*-methoxyacetophenone, 586-37-8; *trans*-stilbene, 103-30-0.

Intramolecular [2 + 2] Photochemical Cycloadditions. 3. Perhydrohistrionicotoxin Synthetic Studies: Synthesis of Spiro[4.5]decanones via Intramolecular [2 + 2] Photocycloaddition[1]

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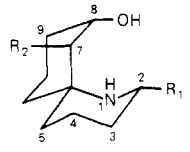
We describe here a full account of our efforts directed toward the synthesis of **4**, a known intermediate in the synthesis of perhydrohistrionicotoxin (**2**). Irradiation of **7** followed by oxidative cleavage of the derived cyclobutene **6** produced **5** or **11**, depending on the method of cyclobutene cleavage. While **5** could not be decarbonylated with $(Ph_3P)_3RhCl$, thermal decarboxylation of **11** furnished **12a** and **12b** with the undesired stereochemistry at C(6) predominating, vis a vis perhydrohistrionicotoxin. Thus, while this strategy does not appear to be viable for perhydrohistrionicotoxin, the photocycloaddition cyclobutene cleavage sequence constitutes a valuable method for the rapid construction of the spiro[4.5]decanone ring system with a high degree of stereocontrol.

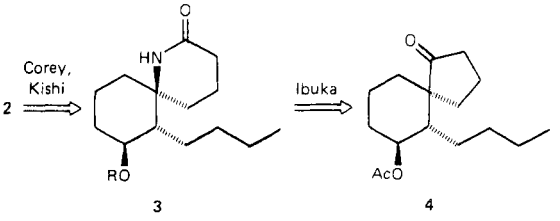
Introduction

Since the initial report in 1971 on the isolation and characterization of histrionicotoxin A (**1**)[3] from the Columbian frog *Dendrobates histrionicus*, it and its perhydro derivative **2**[4] have been the subject of considerable synthetic effort.[5,6] In the perhydro series the majority of approaches converge at spiro lactam **3**, which was first prepared by Corey[7] and Kishi[8] in 1975.



1: R_1 = $CH_2CH{=}CHC{\equiv}CH$ (*cis*); R_2 = $CH{=}CHC{\equiv}CH$ (*cis*)
2: R_1 = *n*-C_5H_{11}; R_2 = *n*-C_4H_9

Our interest in **2** as a synthetic target derived from Ibuka's report[6a,b] on the stereospecific preparation of **4** and its conversion to **3** via the Beckmann rearrangement sequence developed by Corey,[7] in conjunction with our recent



3 4

exploitation of the intramolecular [2 + 2] photocycloaddition of enones to acetylenic moieties.[9] From the

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