20. Photochemical Reactions of Tetrahydroquinoxalin-2(1*H*)-ones and Related Compound

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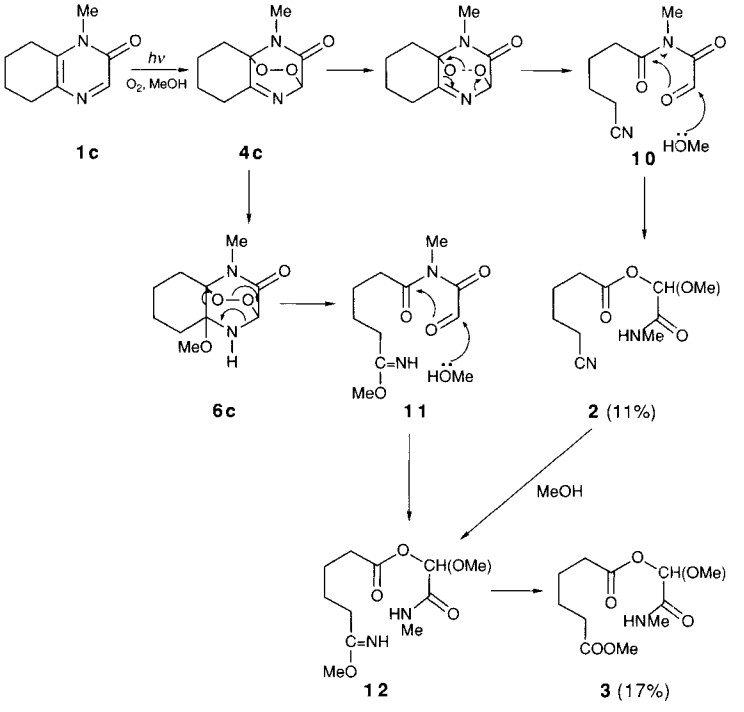
Photochemical behaviors of the pyrazinone derivatives 5,6,7,8-tetrahydroquinoxalin-2(1*H*)-ones **1a–c** and 1,5,6,7,8,9-hexahydro-2*H*-cyclohepta[*b*]pyrazin-2-one **1d** were investigated. Dye-sensitized photo-oxygenation of **1a–c** gave the 1:1 adducts **5a–c** of the corresponding 3,8a-epidioxy-3,5,6,7,8,8a-hexahydroquinoxalin-2(1*H*)-one **4** and H_2O, whereas **1d** gave 3,9a-epidioxy-1,3,5,6,7,8,9,9a-octahydro-2*H*-cyclohepta[*b*]pyrazin-2-one **4d** (*Scheme 2*). The different kind of products was interpreted as being the result of the ring strain and steric hindrance of endoperoxides produced from **1a–d** with singlet oxygen. Irradiation of **1a–b** in the presence of alkenes gave tricyclic azetidine derivatives **9** by [2 + 2] cycloaddition of the C=N bond of **1** to the alkene.

1. Introduction. – The photochemistry of heterocycles possessing an amide functional group such as pyridin-2-ones [1] and uracil derivatives [2] has been extensively studied; however, that of the conjugated cyclohexadienone system containing two N-atoms such as pyrimidinones [3–5], pyrazinones [6] [7], and pyridazinones [8] has received little attention. It is of interest to study the photochemical reactions of cyclic conjugated carbonyl compounds containing N-atoms in view of their relation to nucleoside bases [2]. In earlier work on the photochemical reactivities of cyclic conjugated N–CO systems such as pyrimidinones [3], pyrazinones [6], and quinoxalinones [9], we have demonstrated that the monocyclic pyrazin-2-ones readily reacted with singlet oxygen to form cyclic peroxides [6], while the bicyclic quinoxalin-2-ones underwent [2 + 2] photocycloaddition with alkenes to give tricyclic azetidine derivatives [9]. Therefore, we now examined the photochemical reactions of the bicyclic pyrazinones 5,6,7,8-tetrahydroquinoxalin-2(1*H*)-ones **1a–c** and of the related compound **1d**, in order to understand the generality of these earlier observations.

2. Results and Discussion. – *Photochemical Reactions of* **1** *under Oxygen.* Irradiation of a solution of 1-methyl-5,6,7,8-tetrahydroquinoxalin-2(1*H*)-one (**1c**) in MeOH saturated with O_2 in a *Pyrex* vessel with a high-pressure mercury lamp for 2 h at room temperature gave the two carbamoylmethyl derivatives **2** and **3** in 11 and 17% yield, respectively (*Scheme 1*). The reaction appears to proceed through the intermediate transannular peroxides **4c** or **6c** which undergo O–O bond fission, rearrangement, and addition of MeOH to form carbamoylmethyl cyanopentanoate **2** and carbamoylmethyl methyl hexanedioate **3**. The intermediate endoperoxides **4c** or **6c** could not be isolated in pure form; however, the formation of **6c** was confirmed by the ^{1}H-NMR spectrum (2.98 (*s*, MeN); 3.12 (*s*, MeO); 5.04 ppm (*d*, $J = 3$ Hz, NH)). Ester **3** may be formed by hydrolysis of the methoxyimidoyl group of **12** which derives from **6c** or by methanolysis

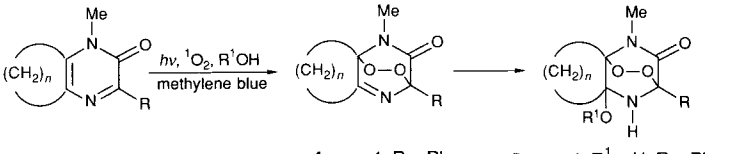
Scheme 1



of intermediate **2**. The formation of endoperoxides from **1c** can be interpreted as photo-oxygenation with singlet oxygen in which **1c** acts as self-sensitizer [6c].

Hence dye-sensitized photo-oxygenation of compounds **1a–d** was performed. As expected, irradiation of 5,6,7,8-tetrahydroquinoxalin-2(1*H*)-ones **1a–c** in CH_2Cl_2 in the presence of methylene blue as sensitizer with visible light at room temperature under O_2 gave the 1:1 adducts of the corresponding endoperoxide **4** and H_2O, *i.e.* 3,8a-epidioxy-octahydro-4a-hydroxyquinoxalin-2(1*H*)-ones **5a–c**, in 41–67% yields after chromatography on silica gel (*Scheme 2, Table*). Similarly, irradiation of **1a** in MeOH under the same conditions gave 3,8a-epidioxy-octahydro-4a-methoxyquinoxalin-2(1*H*)-one **6a** in 61% yield. The structure of endoperoxides **5a–c** and **6a** was elucidated on the basis of their spectral data and elemental analyses, and their formation can be explained by the instability of the endoperoxides **4a–c**, which is due to the ring strain of fused six-membered rings. The same products **5a–c** were obtained when the dye-sensitized photo-oxygenation of **1a–c** was carried out in the presence of molecular sieves to removes traces of H_2O in the solvent: the formation of the endoperoxides **4a–c** was supported by the fact that the reaction mixtures showed a new IR absorption at *ca.* 1630 cm^{-1} (C=N), and thus H_2O addition probably occurred during chromatography on silica gel. On the other hand, dye-sensitized photo-oxygenation of 1,5,6,7,8,9-hexahydro-2*H*-cyclohepta[*b*]pyrazin-2-one **1d** in both CH_2Cl_2 and MeOH under the same condition yielded 3,9a-epidioxy-1,3,5,6,7,8,9,9a-octahydro-2*H*-cyclohepta[*b*]pyrazin-2-one **4d** in 75% yield and no

Scheme 2

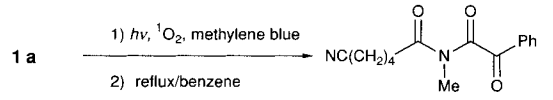


1a *n* = 4, R = Ph
b *n* = 4, R = Et
c *n* = 4, R = H
d *n* = 5, R = Ph

4a *n* = 4, R = Ph
b *n* = 4, R = Et
c *n* = 4, R = H
d *n* = 5, R = Ph

5a *n* = 4, R^1 = H, R = Ph
b *n* = 4, R^1 = H, R = Et
c *n* = 4, R^1 = H, R = H

6a *n* = 4, R^1 = Me, R = Ph



7a (35%)

Table. *Yield of Endoperoxides* **4–6**

Starting material			Solvent	Products (yield [%][a])	
1a	*n* = 4	R = Ph	CH_2Cl_2	**5a** (67)	
1a	*n* = 4	R = Ph	MeOH		**6a** (61)
1b	*n* = 4	R = Et	CH_2Cl_2	**5b** (46)	
1c	*n* = 4	R = H	CH_2Cl_2	**5c** (41)	
1d	*n* = 5	R = Ph	CH_2Cl_2	**4d** (75)	
1d	*n* = 5	R = Ph	MeOH	**4d** (71)	

[a]) Isolated yield.

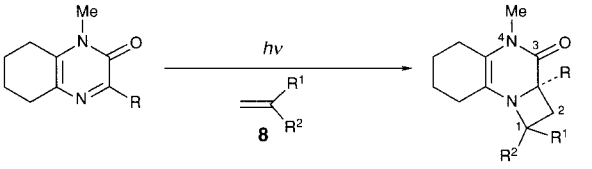
MeOH adduct. This is compatible with the increased stability of **4d** due to less ring strain as a result of the flexibility of the seven-membered ring.

Unsymmetrical cyano-imide **7** was obtained in a one-pot reaction of **1a** [6c]. Dye-sensitized photo-oxygenation of **1a** in benzene, followed by thermal decomposition gave **7** in 35% yield, which corresponds to the intermediate **10** shown in *Scheme 1*.

[2 + 2] Photocycloaddition of the Tetrahydroquinoxalin-2(1H)-ones **1a, b** *to Alkenes* **8**. Recently, we reported that upon irradiation, quinoxalin-2-ones and benzoxazin-2-ones undergo [2 + 2] cycloaddition with electron-poor alkenes [9a,b,d] or arylalkenes [9c] to yield tricyclic azetidines. However, monocyclic pyrazin-2-ones do not react under these conditions with alkenes. Therefore, it is of interest to investigate the photocycloaddition of **1** to alkenes **8** which should reveal the effect of the ring condensed to pyrazin-2-one.

Irradiation of a solution of 5,6,7,8-tetrahydro-3-phenylquinoxalin-2(1*H*)-one **1a** and excess methacrylonitrile in benzene in a *Pyrex* vessel with a high-pressure mercury lamp under Ar at room temperature gave the 1:1 cycloadduct **9a** in 40% yield (*Scheme 3*). The formation of azetidine **9a** was quenched by *trans*-stilbene as a triplet quencher. The structure of **9a** was established by spectral data and elemental analysis. Azetidine **9a** converted back to the starting quinoxalin-2-one **1a** when **9a** was heated at 80°/10^{-3} Torr.

Scheme 3



1a R = Ph
b R = Et

9a R = Ph, R^1 = Me, R^2 = CN; yield 40%[a])
b R = Ph, R^1 = H, R^2 = CN; yield 8%[a])
c R = Ph, R^1 = Me, R^2 = COOMe; yield 16%[a],[b])
d R = R^2 = Ph, R^1 = H; yield 36%[a])
e R = R^2 = Ph, R^1 = Me; yield 38%[a])
f R = R^1 = R^2 = Ph; yield 49%[a])
g R = Et, R^1 = Me, R^2 = CN; yield 25%[a])
h R = Et, R^1 = Me, R^2 = Ph; yield 10%[a])

a) Isolated yield. b) Another stereoisomer was present to 18%.

The ^{1}H-NMR spectrum of **9a** showed newly formed *AB* signals at δ(H) 2.49 (J = 11.7 Hz, 1H) and 3.57 (J = 11.7 Hz, 1H) assignable to a CH_2 group of the azetidine ring. Furthermore, in the ^{13}C-NMR spectrum, signals at δ(C) 45.3 (*t*), 57.1 (*s*), and 64.9 (*s*) due to azetidine-ring C-atoms newly appeared, and the C=N signal of **1a** at δ(C) 148.2 (*s*, C(3)) had disappeared. The regiochemistry of the 1:1 cycloaddition to **9a** was suggested by the chemical shift of the CH_2 group of the azetidine ring [9].

Similarly, upon irradiation, the 5,6,7,8-tetrahydroquinoxalin-2(1*H*)-ones **1a–b** added regioselectively to electron-poor alkenes such as acrylonitrile, methacrylonitrile, and methyl methacrylate or to aryl alkenes such as styrene, α-methylstyrene, and 1,1-diphenylethylene to give azetidine derivatives **9b–h**. In the reaction of **1a** with methyl methacrylate, two stereoisomers were produced. Based on comparison with NMR data of known azetidine derivatives [9], we tentatively assigned structure **9c** to the less abundant one.

Quinoxalin-2(1*H*)-one **1a** did not undergo photocycloaddition to 1,2-disubstituted alkenes such as crotononitrile and methyl crotonate. Irradiation of **1c** in the presence of alkenes gave several unseparable mixtures. Upon irradiation, the 2*H*-cyclohepta[*b*]-pyrazin-2-one **1d** did not undergo cycloaddition to alkenes, and **1d** was recovered unchanged.

The regiospecificity and the lack of stereospecificity in the [2 + 2] photocycloadditions described above suggest that the formation of azetidine derivatives may arise from initial interaction between the quinoxalin-2(1*H*)-one **1** in the triplet state and alkene to give an excited complex as exciplex [10] which subsequently gives a 1,4-biradical intermediate which cyclizes to the azetidine. Based upon the above results and previous observations [9], it appears that ring constraint[1]) and additional conjugation with a electron-withdrawing carbonyl or aryl function at the N- or C-atom [11] are necessary to achieve [2 + 2] photocycloadditions of C=N and C=C bonds.

[1]) Photocycloadditions of simple imines are very rare. Ring constraint due to the incorporation of the C=N function in a ring system, such as six- or five-membered ring, blocks excited-state deactivation by π-bond rotation or N-inversion [11].

Experimental Part

1. *General.* Silica gel (*Merck 60* and *Wakogel C-300* for flash chromatography) was used for column chromatography. M.p.: uncorrected. UV spectra: *Shimadzu-UV-365 spectrophotometer*. IR spectra: *Jasco-IRA-1* spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: *Jeol-FX-100* (100 MHz) spectrometer; in $CDCl_3$ as solvent, using TMS as an internal standard (exceptions noted in parenthesis). Mass spectra: *Hitachi-M-80* spectrometer.

2. *Starting Materials.* The 5,6,7,8-tetrahydroquinoxalin-2(1*H*)-ones **1a–c** and 1,5,6,7,8,9-hexahydro-2*H*-cyclohepta[*b*]pyrazin-2-one (**1d**) were prepared by methylation of the corresponding hydroquinoxalin-2-ol and hydrocycloheptа[*b*]pyrazin-2-ol which were synthesized according to the method previously described [12]. To a stirred soln. of 5,6,7,8-tetrahydroquinoxalin-2-ol or 6,7,8,9-tetrahydro-5*H*-cyclohepta[*b*]pyrazin-2-ol (1 mmol) and NaOMe (from Na (1.1 mmol) and MeOH (5 ml)) in MeOH (15 ml) was added dropwise Me_2SO_4 (1.1 mmol) at r.t. The mixture was refluxed for 1 h, then poured into 10% HCl soln. and extracted with CH_2Cl_2. The extract was washed with 10% $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), and evaporated and the residue chromatographed (silica gel, benzene/AcOEt 10:1 to 2:1 or $CHCl_3$/acetone/EtOH 100:5:1).

5,6,7,8-Tetrahydro-1-methyl-3-phenylquinoxalin-2(1H)-one (**1a**). Yield: 72%. M.p. 136.5–138°. UV (EtOH): 230 (6900), 255 (8300), 364 (14700). IR (KBr): 1640 (C=O). ^{1}H-NMR: 1.70–1.90 (*m*, 4H); 2.50–2.85 (*m*, 4H); 3.48 (*s*, 3H); 7.26–7.46 (*m*, 3H); 8.19–8.32 (*m*, 2H). ^{13}C-NMR: 22.0 (*t*); 26.5 (*t*); 30.1 (*t*); 30.1 (*q*); 127.7 (*d*); 128.6 (*d*); 128.9 (*d*); 130.9 (*s*); 134.4 (*s*); 148.2 (*s*); 155.5 (*s*). Anal. calc. for $C_{15}H_{16}N_2O$: C 74.97, H 6.71, N 11.65; found: C 74.81, H 6.72, N 11.62.

3-Ethyl-5,6,7,8-tetrahydro-1-methylquinoxalin-2(1H)-one (**1b**). Yield: 18%. M.p. 59–60°. UV (EtOH): 231 (4500), 332 (4150). IR (KBr): 1640 (C=O). ^{1}H-NMR: 1.23 (*t*, 3H); 1.65–1.95 (*m*, 4H); 2.50–2.77 (*m*, 4H); 2.80 (*q*, 2H); 3.47 (*s*, 3H). ^{13}C-NMR: 11.2 (*q*); 22.0 (*t*); 26.1 (*t*); 26.9 (*t*); 29.7 (*q*); 29.9 (*t*); 129.8 (*s*); 132.4 (*s*); 155.8 (*s*); 156.8 (*s*). Anal. calc. for $C_{11}H_{16}N_2O$: C 68.71, H 8.38, N 14.57; found: C 68.19, H 8.29, N 14.28.

5,6,7,8-Tetrahydro-1-methylquinoxalin-2(1H)-one (**1c**). Yield: 40%. M.p. 126.5–128°. UV (EtOH): 231 (8300), 340 (6900). IR (KBr): 1650 (C=O). ^{1}H-NMR: 1.66–1.95 (*m*, 4H); 2.50–2.80 (*m*, 4H); 3.48 (*s*, 3H); 8.01 (*s*, 1H). ^{13}C-NMR: 21.7 (*t*); 21.8 (*t*); 26.1 (*t*); 29.5 (*q*); 29.6 (*t*); 131.4 (*s*); 135.0 (*s*); 144.2 (*s*); 156.3 (*s*). Anal. calc. for $C_9H_{12}N_2O$: C 65.83, H 7.36, N 17.06; found: C 65.58, H 7.34, N 16.96.

1,5,6,7,8,9-Hexahydro-1-methyl-3-phenyl-2H-cyclohepta[b]pyrazin-2-one (**1d**). Yield: 73%. M.p. 104–105°. UV (EtOH): 230 (8200), 257 (7900), 369 (14400). IR (KBr): 1630 (C=O). ^{1}H-NMR: 1.56–2.00 (*m*, 6H); 2.75–3.05 (*m*, 4H); 3.62 (*s*, 3H); 7.26–7.55 (*m*, 3H); 8.20–8.37 (*m*, 2H). ^{13}C-NMR: 24.8 (*t*); 26.1 (*t*); 29.6 (*t*); 31.3 (*q*); 31.6 (*t*); 36.0 (*t*); 127.8 (*d*); 128.6 (*d*); 128.9 (*d*); 136.4 (*s*); 136.7 (*s*); 140.3 (*s*); 146.8 (*s*); 155.3 (*s*). Anal. calc. for $C_{16}H_{18}N_2O$: C 75.56, H 7.13, N 11.01; found: C 75.40, H 7.13, N 10.95.

3. *Photoreaction of* **1c**. A soln. of **1c** (200 mg) in MeOH (50 ml) was irradiated in a *Pyrex* vessel with a Hg high-pressure lamp (450 W) under O_2 for 5 h at r.t. After evaporation, the residual oil was chromatographed (silica-gel column, $CHCl_3$/acetone/EtOH 100:10:2): **2** and **3**. These products could not be completely separated in anal. pure form by column chromatography on silica gel.

Methoxy(methylcarbamoyl)methyl 5-Cyanopentanoate (**2**). Oil. IR ($CHCl_3$): 3430, 2225, 1740, 1685. ^{1}H-NMR: 1.65–1.94 (*m*, 4H); 2.30–2.57 (*m*, 4H); 2.85 (*d*, J = 4.9, 3H); 3.53 (*s*, 3H), 5.91 (*s*, 1H); 6.69 (br. *s*, 1H, exchangeable with D_2O). ^{13}C-NMR: 17.0 (*t*); 23.7 (*t*); 24.7 (*t*); 26.0 (*q*); 33.1 (*t*); 57.9 (*q*); 93.6 (*d*); 119.4 (*s*); 166.2 (*s*); 172.1 (*s*). CI-MS: 229 ([M + 1]$^+$).

Methoxy(methylcarbamoyl)methyl Methyl Hexanedioate (**3**). Oil. IR ($CHCl_3$): 3430, 1730, 1685. ^{1}H-NMR: 1.63–1.77 (*m*, 4H); 2.24–2.53 (*m*, 4H); 2.86 (*d*, J = 5.4, 3H); 3.53 (*s*, 3H); 3.67 (*s*, 3H); 5.92 (*s*, 1H); 6.67 (br. *s*, 1H, exchangeable with D_2O). ^{13}C-NMR: 24.0 (*t*); 24.1 (*t*); 25.8 (*q*); 33.5 (*t*); 33.6 (*t*); 51.4 (*q*); 57.4 (*q*); 93.3 (*d*); 166.1 (*s*); 172.4 (*s*); 173.5 (*s*). CI-MS: 262 ([M + 1]$^+$).

4. *Dye-Sensitized Photo-oxygenation of* **1**. An oxygenated soln. of **1** (200 mg) in CH_2Cl_2 or MeOH (70 ml) in the presence of methylene blue as a sensitizer was irradiated in a *Pyrex* tube with a halogen lamp for 1 h at r.t. The sensitizer was filtered off through silica gel, the solvent evaporated, and the residue chromatographed (silica-gel column, benzene/AcOEt 4:1 to 1:9).

3,9a-Epidioxy-1,3,5,6,7,8,9,9a-octahydro-1-methyl-3-phenyl-2H-cyclohepta[b]pyrazin-2-one (**4d**). M.p. 131.4–133°. IR (KBr): 1700, 1625. ^{1}H-NMR: 1.59–2.00 (*m*, 6H); 2.05–2.32 (*m*, 2H); 2.58–2.90 (*m*, 2H); 2.99 (*s*, 3H); 7.37–7.49 (*m*, 3H); 7.77–7.91 (*m*, 2H). ^{13}C-NMR: 23.4 (*t*); 26.4 (*q*); 26.7 (*t*); 29.2 (*t*); 30.9 (*t*); 37.6 (*t*); 89.1 (*s*); 91.2 (*s*); 128.0 (*d*); 128.8 (*d*); 129.9 (*d*); 130.9 (*d*); 169.9 (s); 182.6 (*s*). Anal. calc. for $C_{16}H_{18}N_2O_3$: C 67.11, H 6.33, N 9.78; found: C 66.94, H 6.30, N 9.79.

3,8a-Epidioxy-3,4,4a,5,6,7,8,8a-octahydro-4a-hydroxy-1-methyl-3-phenylquinoxalin-2(1H)-one (**5a**). M.p. 130.5–131.5° (dec.). IR (KBr): 3440, 3320. ^{1}H-NMR: 1.55–1.80 (*m*, 4H); 1.80–2.12 (*m*, 4H); 2.69 (*s*, 1H, exchangeable with D_2O); 3.01 (*s*, 3H); 3.35 (br. *s*, 1H, exchangeable with D_2O); 7.34–7.60 (*m*, 5H). ^{13}C-NMR:

20.3 (*t*); 20.5 (*t*); 26.5 (*t*); 26.8 (*q*); 35.6 (*t*); 79.7 (*s*); 90.2 (*s*); 90.9 (*s*); 126.6 (*d*); 128.2 (*d*); 129.2 (*d*); 132.0 (*s*); 166.3 (*s*). Anal. calc. for $C_{15}H_{18}N_2O_4$: C 60.06, H 6.25, N 9.65; found: C 61.86, H 6.27, N 9.55. CI-MS: 291 ($[M + 1]^+$).

3,8a-Epidioxy-3-ethyl-3,4,4a,5,6,7,8,8a-octahydro-4a-hydroxy-1-methylquinoxalin-2(1H)-one (**5b**). M.p. 144–145° (dec.). IR (KBr): 3420, 3340, 1710, 1690. ^{1}H-NMR ((D$_6$)DMSO): 0.94 (*t*, 3H); 1.30–1.97 (*m*, 10 H); 2.85 (*s*, 3H); 4.43 (*s*, 1H); 5.24 (*s*, 1H). ^{13}C-NMR ((D$_6$)DMSO): 7.87 (*q*); 20.4 (*t*); 23.5 (*t*); 26.0 (*t*); 26.0 (*q*); 35.5 (*t*); 78.8 (*s*); 89.5 (*s*); 90.0 (*s*); 166.1 (*s*). Anal. calc. for $C_{11}H_{18}N_2O_4$: C 54.53, H 7.48, N 11.56; found: C 54.24, H 7.44, N 11.44.

3,8a-Epidioxy-3,4,4a,5,6,7,8,8a-octahydro-4a-hydroxy-1-methylquinoxalin-2(1H)-one (**5c**). IR (KBr): 3370, 3300, 1710. ^{1}H-NMR ((D$_6$)DMSO): 1.14–2.15 (*m*, 8H); 2.85 (*s*, 3H); 4.86 (*d*, J = 4.4, 1H, exchangeable with D$_2$O); 5.00 (*d*, J = 4.4, 1H); 5.37 (*s*, 1H, exchangeable with D$_2$O). ^{13}C-NMR ((D$_6$)DMSO): 20.1 (*t*); 20.4 (*t*); 25.8 (*t*); 25.8 (*q*); 35.4 (*t*); 78.6 (*s*); 84.9 (*d*); 90.6 (*s*); 165.2 (*s*). CI-MS: 215 ($[M + 1]^+$).

3,8a-Epidioxy-3,4,4a,5,6,7,8,8a-octahydro-4a-methoxy-1-methyl-3-phenylquinoxalin-2(1H)-one (**6a**). M.p. 147–148° (dec.). IR (KBr): 3280, 1695. ^{1}H-NMR: 1.38–1.98 (*m*, 6H); 1.98–2.50 (*m*, 2H); 2.80 (br. *s*, 1H, exchangeable with D$_2$O); 3.02 (*s*, 3H); 3.22 (*s*, 3H); 7.28–7.60 (*m*, 5H). ^{13}C-NMR: 20.2 (*t*); 20.4 (*t*); 26.5 (*t*); 26.9 (*q*); 30.5 (*t*); 46.9 (*q*); 83.6 (*s*); 90.1 (*s*); 90.3 (*s*); 126.7 (*d*); 128.2 (*d*); 129.5 (*d*); 132.8 (*s*); 166.0 (*s*). Anal. calc. for $C_{16}H_{20}N_2O_4$: C 63.14, H 6.62, N 9.20; found: C 63.01, H 6.63, N 9.10. CI-MS: 305 ($[M + 1]^+$).

5. *Imide* **7** *by Dye-Sensitized Photo-oxygenation of* **1a** *Followed by Thermolysis.* An oxygenated soln. of **1a** (100 mg) in CH_2Cl_2 (70 ml) in the presence of methylene blue (*ca.* 2 mg) as sensitizer was irradiated for 1 h under the same conditions as described above. The sensitizer was filtered off, the solvent evaporated, and the mixture dissolved in benzene (30 ml) and refluxed for 2 h. Usual workup gave *5-cyano-*N*-methyl-*N*-(2-oxo-2-phenylethanoyl)pentanamide* (**7**; 40 mg, 35%). IR ($CHCl_3$): 2225, 1710, 1685. ^{1}H-NMR: 1.56–1.88 (*m*, 4H); 2.19–2.38 (*m*, 2H); 2.52–2.72 (*m*, 2H); 3.33 (*s*, 3H); 7.32–7.62 (*m*, 3H); 7.74–7.87 (*m*, 2H). ^{13}C-NMR: 16.8 (*t*); 22.5 (*t*); 24.4 (*t*); 29.7 (*q*); 34.3 (*t*); 119.2 (*s*); 128.7 (*d*); 128.9 (*d*); 132.5 (*s*); 133.9 (*d*); 169.9 (*s*); 174.7 (*s*); 187.0 (*s*). CI-MS: 273 ($[M + 1]^+$).

6. *General Procedure for the Photocycloaddition of* **1a,b** *to Alkenes.* A soln. of **1a,b** (200 mg) and alkene (*ca.* 2 ml) in benzene (70 ml) was irradiated in a *Pyrex* vessel with a Hg high-pressure lamp under Ar for 2–12 h at r.t. After removal of the solvent, the residual oil was chromatographed (silica-gel column, benzene/AcOEt 10:1 or benzene only) to give the azetidine derivatives **9**.

2,2a,3,4,5,6,7,8-Octahydro-1,4-dimethyl-3-oxo-2a-phenyl-1H-azeto[1,2-a]quinoxaline-1-carbonitrile (**9a**). M.p. 141–142°. IR (KBr): 2220, 1670, 1650. ^{1}H-NMR: 1.23–2.36 (*m*, 8H); 1.69 (*s*, 3H); 2.49, 3.57 (*AB*, J = 11.7, 2H); 3.09 (*s*, 3H); 7.22–7.60 (*m*, 5H). ^{13}C-NMR: 21.6 (*t*); 22.4 (*t*); 25.6 (*t*); 27.7 (*t*); 28.3 (*q*); 28.7 (*q*); 45.3 (*t*); 57.1 (*s*); 64.9 (*s*); 119.4 (*s*); 119.7 (*s*); 124.9 (*d*); 125.6 (*s*); 127.7 (*d*); 128.4 (*d*); 141.4 (*s*); 166.6 (*s*). CI-MS: 308 ($[M + 1]^+$). Anal. calc. for $C_{19}H_{21}N_3O$: C 74.23, H 6.88, N 13.66; found: C 73.89, H 6.83, N 13.64.

2,2a,3,4,5,6,7,8-Octahydro-4-methyl-3-oxo-2a-phenyl-1H-azeto[1,2-a]quinoxaline-1-carbonitrile (**9b**). IR (KBr): 2240, 1670, 1645. ^{1}H-NMR: 1.20–2.45 (*m*, 8H); 3,10 (*s*, 3H); 2.90 (*A* of *ABX*, J = 8.3, 11.7, 1H); 3.37 (*B* of *ABX*, J = 2.9, 11.7, 1H); 4.49 (*X* of *ABX*, J = 2.9, 8.3, 1H); 7.22–7.59 (*m*, 5H). ^{13}C-NMR: 21.4 (*t*); 22.5 (*t*); 25.5 (*t*); 26.1 (*t*); 28.7 (*q*); 37.3 (*t*); 48.1 (*d*); 68.4 (*s*); 117.1 (*s*), 119.4 (*s*); 124.9 (*d*); 126.0 (*s*); 127.9 (*d*); 128.5 (*d*); 141.0 (*s*); 166.4 (*s*). CI-MS: 294 ($[M + 1]^+$).

Methyl 2,2a,3,4,5,6,7,8-Octahydro-1,4-dimethyl-3-oxo-2a-phenyl-1H-azeto[1,2-a]quinoxaline-1-carboxylate (**9c**). The 2 stereoisomers present could not be completely separated. Isomer **9c** (16%). IR ($CHCl_3$): 1730, 1630. ^{1}H-NMR: 1.08–2.40 (*m*, 8H); 1.51 (*s*, 3H); 2.87, 3.08 (*AB*, J = 12.0, 2H); 3.07 (*s*, 3H); 3.75 (*s*, 3H); 7.21–7.60 (*m*, 5H). ^{13}C-NMR: 20.8 (*q*); 21.8 (*t*); 22.7 (*t*); 25.6 (*t*); 27.6 (*t*); 28.5 (*q*); 43.7 (*t*); 52.1 (*q*); 64.1 (*s*); 64.8 (*s*); 120.3 (*s*); 122.9 (*s*); 125.2 (*d*); 127.2 (*d*); 128.3 (*d*); 142.1 (*s*); 167.6 (*s*); 174.7 (*s*). CI-MS: 341 ($[M + 1]^+$). Stereoisomer (18%). IR ($CDCl_3$): 1720, 1645. ^{1}H-NMR: 1.20–2.23 (*m*, 8H); 1.57 (*s*, 3H); 2.30, 3.61 (*AB*, J = 12.0, 2H); 3.02 (*s*, 3H); 3.72 (*s*, 3H); 7.19–7.40 (*m*, 5H). CI-MS: 341 ($[M + 1]^+$).

2a,4,5,6,7,8-Hexahydro-4-methyl-1,2a-diphenyl-1H-azeto[1,2-a]quinoxalin-3(2H)-one (**9d**). IR ($CHCl_3$): 1635. ^{1}H-NMR: 1.17–2.35 (*m*, 8H); 2.36 (*A* of *ABX*, J = 7.8, 10.8, 1H); 3.08 (*s*, 3H); 4.76 (*B* of *ABX*, J = 7.8, 11.2, 1H); 4.76 (*X* of *ABX*, J = 7.8, 1H); 7.18–7.70 (*m*, 10H). ^{13}C-NMR: 21.8 (*t*); 22.7 (*t*); 25.5 (*t*); 27.0 (*t*); 28.5 (*q*); 43.7 (*t*); 64.5 (*d*); 65.1 (*s*); 120.9 (*d*); 124.2 (*s*); 125.3 (*d*); 126.6 (*d*); 127.1 (*d*); 127.5 (*d*); 127.7 (*d*); 128.0 (*d*); 128.3 (*d*); 142.9 (*s*); 143.5 (*s*); 167.8 (*s*). CI-MS: 345 ($[M + 1]^+$).

2a,4,5,6,7,8-Hexahydro-1,4-dimethyl-1,2a-diphenyl-1H-azeto[1,2-a]quinoxalin-3(2H)-one (**9e**). IR (KBr): 1670, 1645. ^{1}H-NMR: 1.18–2.37 (*m*, 8H); 1.70 (*s*, 3H); 2.90, 3.23 (*AB*, J = 11.2, 2H); 3.09 (*s*, 3H); 7.05–7.68 (*m*, 10H). ^{13}C-NMR: 21.7 (*t*); 22.7 (*t*); 23.4 (*t*); 25.6 (*t*); 27.9 (*q*); 28.5 (*q*); 49.7 (*t*); 63.8 (*s*); 65.2 (*s*); 121.1 (*s*); 121.5 (*s*); 125.1 (*d*); 125.3 (*d*); 126.9 (*d*); 128.2 (*d*); 143.1 (*s*); 148.3 (*s*); 168.0 (*s*). CI-MS: 359 ($[M + 1]^+$).

2a,4,5,6,7,8-Hexahydro-4-methyl-1,1,2a-triphenyl-1H-azeto[1,2-a]quinoxalin-3(2H)-one (**9f**). M.p. 143–144°. IR ($CHCl_3$): 1640. ^{1}H-NMR: 1.05–2.30 (*m*, 8H); 2.68 (*s*, 3H); 2.70, 4.20 (*AB*, J = 12.2, 2H); 7.05–7.78 (*m*, 15H). ^{13}C-NMR: 21.5 (*t*); 22.4 (*t*); 25.2 (*t*); 28.0 (*q*); 28.9 (*t*); 47.4 (*t*); 64.5 (*s*); 73.7 (*s*); 121.2 (*s*); 124.0 (*s*); 125.3 (*d*); 126.4 (*d*); 127.0 (*d*); 127.4 (*d*); 127.5 (*d*); 127.8 (*d*); 128.2 (*d*); 140.2 (*s*); 142.7 (*s*); 148.2 (*s*); 168.0 (*s*). CI-MS: 421 ($[M + 1]^+$).

2a-Ethyl-2,2a,3,4,5,6,7,8-octahydro-1,4-dimethyl-3-oxo-1H-azeto[1,2-a]quinoxaline-1-carbonitrile (**9g**). IR ($CHCl_3$): 2240, 1640. ^{1}H-NMR: 0.91 (*t*, 3H); 1.26–2.10 (*m*, 8H); 1.63 (*s*, 3H); 2.16–2.38 (*s*, 2H); 2.33, 3.07 (*AB*, J = 11.7, 2H); 3.12 (*s*, 3H). ^{13}C-NMR: 7.2 (*q*); 21.3 (*t*); 22.3 (*t*); 25.4 (*t*); 27.4 (*t*); 28.1 (*t*); 28.1 (*q*); 32.1 (*q*); 41.2 (*t*); 57.0 (*s*); 63.9 (*s*); 119.4 (*s*); 120.0 (*s*); 124.0 (*s*); 168.2 (*s*). CI-MS: 260 ($[M + 1]^+$).

2a-Ethyl-2a,4,5,6,7,8-hexahydro-1,4-dimethyl-1-phenyl-1H-azeto[1,2-a]quinoxalin-3(2H)-one (**9h**). IR ($CHCl_3$): 1630. ^{1}H-NMR: 0.93 (*t*, 3H); 1.08–2.10 (*m*, 8H); 2.10–2.39 (*m*, 3H); 2.81 (*d*, J = 11.2, 1H); 3.15 (*s*, 3H); 7.05–7.45 (*m*, 3H); 7.50–7.70 (*m*, 2H). ^{13}C-NMR: 8.1 (*q*); 21.7 (*t*); 22.8 (*t*); 24.0 (*q*); 25.7 (*t*); 28.2 (*t*); 28.2 (*q*); 33.2 (*t*); 46.6 (*t*); 62.8 (*s*); 64.8 (*s*); 120.5 (*s*); 121.8 (*s*); 124.8 (*d*); 126.3 (*d*); 128.0 (*d*); 149.1 (*s*); 169.8 (*s*). CI-MS: 311 ($[M + 1]^+$).

7. *Quenching Experiment of the Photocycloaddition of* **1a** *to Methacrylonitrile.* A soln. of **1a** (0.5 mmol), methacrylonitrile (8 mmol), and *trans*-stilbene (2 mmol) in benzene (40 ml) was irradiated at 366 nm, which was isolated with a filter soln. of naphthalene (3 g/500 ml MeOH). The photocycloaddition was completely quenched.

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