(100 MHz) ($CDCl_3$) 1.34–1.68 (m, 6 H, CH_2), 3.02 (t, 2 H, N-CH_2), 3.35 (s, 2 H, NH and OH), 3.52 (t, 2 H, CH_2OH), 6.51–7.21 (m, 5 H, Ph); ^{13}C NMR (25.05 MHz) ($CDCl_3$) 23.3 (t, CH_2), 29.1 (t, CH_2), 32.3 (t, CH_2), 43.8 (t, N-CH_2), 62.2 (t, O-CH_2), 112.8 (d), 117.1 (d), 129.1 (d), 148.3 (s). Anal. Found: C, 73.92; H, 9.80; N, 7.57; O, 9.09. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81; O, 8.93.

Supplementary Material Available: NMR data and analyses of 1-(4-methylphenyl)piperidine, 1-(3-methylphenyl)piperidine, 1-(2-methylphenyl)piperidine, 1-(4-methoxyphenyl)piperidine, 1-(2-methoxyphenyl)piperidine, 1-(4-chlorophenyl)piperidine, 1-(2-chlorophenyl)piperidine, 1-octylpiperidine, 1-(phenylethyl)piperidine, 1-cyclohexylpiperidine, 1-benzylpiperidine, 4-phenylmorpholine, 4-(4-chlorophenyl)morpholine, 4-(2-methoxyphenyl)morpholine, 4-(4-methoxyphenyl)morpholine, 4-(2-methylphenyl)morpholine, 4-(4-methylphenyl)morpholine, 4-laurylmorpholine, *N*-methyl-*N'*-phenylpiperazine, *N*,*N'*-diphenylpiperazine (6 pages). Ordering information is given on any current masthead page.

Photocycloaddition Reactions of 1,4-Benzoxazin-2-ones and Electron-Poor Olefins

Takehiko Nishio* and Yoshimori Omote

Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaraki 305, Japan

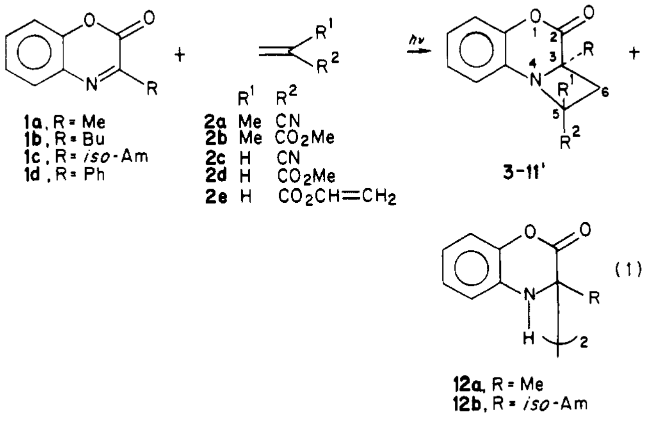
Received September 18, 1984

The photochemical reactivity of 1,4-benzoxazin-2-ones **1** with electron-poor olefins **2** such as cyanoolefins and vinyl carboxylates is described. Irradiation of 1,4-benzoxazin-2-ones **1a–c** in the presence of electron-poor olefins **2a–e** afforded azetidine derivatives **3–11'** via (2 + 2) photocycloaddition of the carbon–nitrogen double bond of **1** to olefin. The photoreaction of the 1,4-benzoxazin-2-one **1a** with olefin **2a** occurs from a triplet state.

Although (2 + 2) photocycloadditions of olefins to carbon-carbon[1,2] and carbon–oxygen double bonds[2,3] are common, synthetically useful reactions, similar photocycloadditions to the carbon–nitrogen double bond are rare and are known only for cyclic imines, which are conjugated with imino[4] and carbonyl groups[5–7] on both nitrogen and carbon atoms, and a heteroatom such as nitrogen[4,6] and oxygen[8] on the nitrogen atom. Recently, an additional case has been shown by Ohta et al.[9] that 6-cyanophenanthridine underwent photocycloaddition with electron-rich olefins to give the expected four-membered ring compounds. In view of the limited occurrence of photocycloaddition to the C=N double bond linkage, we have investigated the generality of this process in quinoxalinones.[7] We report here the photocycloaddition of the 1,4-benzoxazin-2-ones **1** to electron-poor olefins **2**.

Irradiation of a mixture of 3-methyl-1,4-benzoxazin-2-one (**1a**) and an excess of methacrylonitrile (**2a**) in benzene with a high-pressure mercury lamp through a Pyrex filter under a nitrogen atmosphere at room temperature for 15 h gave two stereoisomeric azetidine derivatives (**3** and **3'**) in 11% and 74% isolated yields, respectively. The structures for these photoproducts were supported by elemental analyses as well as their spectroscopic properties. Characteristically, these photocycloadducts and others to be described show a carbonyl stretch at around 1760 cm^{-1} and no carbon–nitrogen double bond in the infrared spectrum.

The regiochemistry of cycloaddition was suggested by the chemical shifts of the azetidine ring methylene protons of the (2 + 2) photocycloadducts.[10] Thus the azetidine **3** showed methylene protons at δ 2.94 (d, 1 H, J = 12.2 Hz) and 3.15 (d, 1 H, J = 12.2 Hz) and **3'** showed methylene protons at δ 2.59 (d, 1 H, J = 12.2 Hz) and 3.29 (d, 1 H, J = 12.2 Hz).[10] The stereochemistry of the photocycloadducts **3** and **3'** was assigned as shown in eq 1 on the basis



---

(1) Baldwin, S. W. "Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 123.

(2) Turro, N. J. "Modern Molecular Photochemistry"; Benjamin/Cummings: Melano Park, CA, 1978; p 415.

(3) Jones, G., II. "Photochemistry"; Padwa, A., Ed.; Marcel Dekker: New York, 1981; Vol. 5, p 1.

(4) Tsuge, O.; Tashiro, M.; Oe, K. *Tetrahedron Lett.* **1968**, 3971. Tsuge, O.; Oe, K.; Tashiro, M. *Tetrahedron* **1973**, *29*, 41. Oe, K.; Tashiro, M.; Tsuge, O. *Bull. Chem. Soc. Jpn* **1977**, *50*, 3281.

(5) Howard, K. A.; Koch, T. H. *J. Am. Chem. Soc.* **1975**, *97*, 7288. Rodehorst, M.; Koch, T. H. *Ibid.* **1975**, *97*, 7298. Koch, T. H.; Higgins, R. H.; Schuster, H. F. *Tetrahedron Lett.* **1977**, 431.

(6) Swenton, J. C.; Hyatt, J. A. *J. Am. Chem. Soc.* **1974**, *96*, 4879.

(7) Nishio, T. *J. Org. Chem.* **1984**, *49*, 827.

(8) Kumagai, T.; Shimizu, K.; Kawamura, Y.; Mukai, T. *Tetrahedron* **1981**, *37*, 3365.

(9) Futamura, S.; Ohta, H.; Kamiya, Y. *Bull. Chem. Soc. Jpn.* **1980**, *55*, 2190.

(10) Batterham, T. J. "NMR Spectra of Simple Heterocycles"; Taylor, E. C., Weissberger, A., Eds.; Wiley: New York, 1973; p 144. Chemical shifts of methylene protons of another regioisomer (3'') would be at lower field due to the electronegativity of adjacent nitrogen.

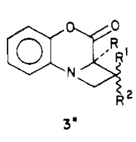

3''

Table I. Yield of (2 + 2) Photocycloadducts 3–11′

				yield,[a] %	
product	R	R^1	R^2	1:1 cycloadduct	recovered
3	Me	Me	CN	11	
3′	Me	CN	Me	74	trace
4	Me	Me	CO_2Me	15	
4′	Me	CO_2Me	Me	43	trace
5	Me	H	CN	36	
5′	Me	CN	H	29	trace
6	Me	H	CO_2Me		
6′	Me	CO_2Me	H	41[b]	35
7	Me	H	$CO_2CH{=}CH_2$	20	45
8	Bu	Me	CN	75	trace
9	Bu	Me	CO_2Me	59	trace
10	*iso*-Am	Me	CN	11	
10′	*iso*-Am	CN	Me	38	trace; **12b**, 5
11	*iso*-Am	Me	CO_2Me	19	
11′	*iso*-Am	CO_2Me	Me	68	trace; **12b**, 1

[a] Isolated yield. [b] **6** and **6′** were not completely separated. **6**:**6′** = 1:2 by NMR.

Table II. Photoreactions of the 1,4-Benzoxazin-2-one 1a[a] in the Presence of Methacrylonitrile 2a under Various Conditions

				yield of 1:1 cycloadducts,[b] %			
run	solvnt	irradiatn time, h	conditns	**3**	**3′**	recovd **1a**	
1	benzene	3	N_2, >300 nm	11	34	44	
2	benzene	15	N_2, >300 nm	11	74	trace	
3	acetone	3	N_2, >300 nm	6	25	68	
4	acetone	15	N_2, >300 nm	7	71	trace	
5	MeOH	15	N_2, >300 nm	6	35	trace	
6	CH_3CN	15	N_2, >300 nm	4	39	trace	
7	benzene	3	N_2, 366 nm[d]	17	82	~0	
8	benzene	3	O_2,[c] 366 nm[d]	trace	trace	92	
9	benzene	3	N_2, 366 nm[d] thioxanthone[e]	10	76	trace	
10	benzene	3	N_2, 366 nm,[d] Michler's ketone[e]	ND[h]	16	10	dimer **12a**, 33
11	benzene	3	N_2, 366 nm,[d] *trans*-stilbene[f]	ND[h]	ND[h]	96	
12[g]	benzene	3	N_2, 366 nm[d]	ND[h]	ND[h]	~100	
13[g]	benzene	3	N_2, 366 nm,[d] Michler's ketone[e]	*i*	*i*	20	dimer **12a**, 38

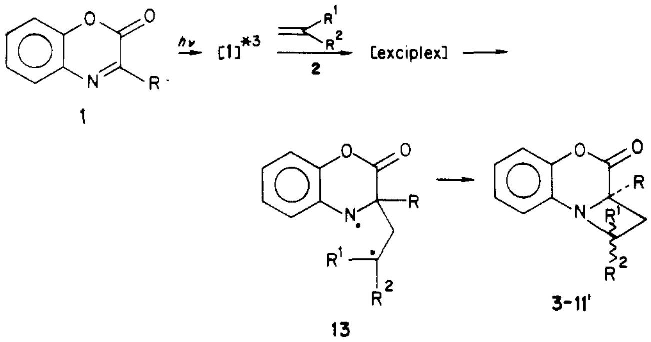
[a] UV spectrum of **1a**: λ_{max} (EtOH) 209 (ϵ 14 800), 284 (8600), and 313 nm (6000). **1a** showed an end absorption until 370 nm (ϵ 250 at 366 nm). [b] Isolated yield. [c] Oxygen was bubbling during irradiation. [d] A Pyrex glass filter and a methanol solution of naphthalene (5 g/1 L) were used to isolate the 366-nm region. [e] A sensitizer absorbed more than 95% light. [f] UV spectrum of *trans*-stilbene shows no absorption at 366 nm and 10 molar equiv of *trans*-stilbene was used. [g] In the absence of methacrylonitrile (**2a**). [h] Not detected. [i] Not isolated.

of the NMR spectrum. The C-5 methyl protons (δ 1.49) in the azetidine ring of **3** appeared as a singlet at higher field than those (δ 1.79) of the other stereoisomer **3′** due to the anisotropic effect of the benzene ring. Additional evidence for the stereochemical assignment appears in the ^{13}C NMR spectrum. The C-5 methyl carbon signal (21.8 ppm) in the azetidine ring of **3** appeared upfield from the corresponding signal (28.0 ppm) of the stereoisomer **3′**. Irradiation of the 1,4-benzoxazin-2-ones **1a–c** in benzene in the presence of cyanoolefins **2a,c** under the same conditions as described above gave the (2 + 2) photocycloadducts **5**, **5′**, **8**, **10**, and **10′** (Table I). Intramolecular hydrogen abstraction reaction by carbonyl oxygen or imono nitrogen was not observed when the 1,4-benzoxazin-2-ones (**1b,c**), which possess hydrogens to be abstracted in the side chain at C-3, were irradiated. The good yield in the (2 + 2) photocycloaddition of the 1,4-benzoxazin-2-ones **1** to cyanoolefins **2** prompted us to examine the photoaddition of **1** to acrylate derivatives. So far in the Paterno–Büchi reaction,[3] it has been reported that ketones do not undergo the photocycloaddition with electron-poor olefins such as methyl methacrylate, methyl acrylate, and vinyl acetate.

Irradiation of 3-methyl-1,4-benzoxazin-2-one (**1a**) in benzene in the presence of an excess methyl methacrylate (**2b**) under the same conditions as described above yielded two stereoisomeric photocycloadducts, **4** and **4′**, in 15% and 43% yields, respectively. The structure and regiochemistry of the photocycloadducts were elucidated on the basis of the usual spectroscopic and analytical data (Experimental Section). The stereochemistry was based upon the chemical shifts of methyl protons in the NMR spectrum. The C-5 methyl and methoxycarbonyl methyl protons of the photocycloadduct **4** appeared as two singlets at δ 1.34 (3 H) and 3.85 (3 H), respectively. Those of other stereoisomer **4′** appeared at δ 1.73 (3 H) and 3.42 (3 H). Similarly, irradiation of a solution of the 1,4-benzoxazin-2-ones **1a–c** in benzene-containing acylate derivatives **2b,d,e** gave photocycloadducts **6**, **6′**, **7**, **9**, **11**, and **11′** in 11–63% yields (Table I). However, irradiation of 3-phenyl-1,4-benzoxazin-2-one (**1d**) in benzene in the presence of cyanoolefins **2a,c** or vinyl carboxylates **2b,d** gave no photocycloadducts and **1d** was recovered quantitatively, probably due to the steric factor of the phenyl group at C-3 of **1d**.

Irradiation of a mixture of the 1,4-benzoxazin-2-one (**1a**) and β-substituted electron-poor olefins such as crotononitrile or methyl crotonate gave small amounts of several unseparable mixtures and the corresponding photocycloadducts could not be isolated. The formation of the photocycloadducts **3** and **3′** was completely quenched by oxygen and *trans*-stilbene as triplets quenchers (Table II, runs 8 and 11). The isolated amount of the photocycloadducts **3** and **3′** was constant within experimental error when a mixture of the 1,4-benzoxazin-2-one (**1a**) and methacrylonitrile (**2a**) was irradiated in acetone or in the presence of thioxanthone as a triplet sensitizer (runs 3, 4, and 9). These results suggest that the photoaddition occurs from the excited triplet state of the 1,4-benzoxazin-2-one (**1a**). However, when Michler's ketone was used as a triplet sensitizer, the reaction was not clean and the

Scheme I



reductive dimer **12a** was obtained as main photoproduct. The reductive dimer **12a** was also produced when a mixture of **1a** and Michler's ketone in benzene even in the absence of **2a**.[11] The regioselectivity and nonsterospecificity of (2 + 2) photocycloaddition suggest that the formation of the azetidine derivatives **3–11′** may arise by initial interaction of the 1,4-benzoxazin-2-one triplet with the electron-poor olefins **2** to give an excited complex or exciplex,[12] which proceeds to give 1,4-diradical intermediate **13**[7] and then this 1,4-diradical cyclizes to give the final products (Scheme I).

Experimental Section

Melting and boiling points are uncorrected. Melting points were measured with Yanaco micro melting point apparatus (MP-J3) and boiling points were measured with Büchi Kugelrohr (KR-3) apparatus. UV spectra were recorded on a JASCO UVIDEC-505 spectrometer and IR spectra were determined with a Hitachi 260-30 spectrometer. ^{1}H and ^{13}C NMR spectra were run on a JEOL FX 100 spectrometer (100 MHz) using $CDCl_3$ as solvent. Mass spectra were measured with a Hitachi M-80 spectrometer. A HALōs (Eikosha EHP-300 W) high-pressure mercury lamp was used as an irradiation source.

Materials. 1,4-Benzoxazin-2-ones **1a** and **1d** were prepared according to methods previously described in the literature,[13,14] and **1b** and **1c** were prepared by a modification of these methods.

3-Methyl-1,4-benzoxazin-2-one (1a): mp 100.5–102 °C (lit.[13] mp 101–103 °C); UV (EtOH) 209 (ϵ 14 800), 284 (8600), 313 nm (6000); IR (KBr) 1720, 1605, 1215, 1115, 1090, 755 cm^{-1}; ^{1}H NMR δ 2.56 (s, 3 H), 7.20–7.49 (m, 3 H), 7.65–7.74 (m, 1 H); ^{13}C NMR 21.3 (q), 116.3 (d), 125.6 (d), 128.6 (d), 130.5 (d), 131.0 (s), 146.5 (s), 153.1 (s), 155.1 ppm (s).

3-Butyl-1,4-benzoxazin-2-one (1b): mp 67–68 °C; UV (EtOH) 210 (ϵ 14 300), 284 nm (9000); IR (KBr) 1725, 1610, 1195, 1120, 1075, 775, 755, 700 cm^{-1}; ^{1}H NMR δ 0.98 (t, 3 H), 1.28–1.93 (m, 4 H), 2.89 (t, 2 H), 7.20–7.55 (m, 3 H), 7.67–7.77 (m, 1 H); ^{13}C NMR 13.9 (q), 22.5 (t), 28.4 (t), 33.9 (t), 116.2 (d), 125.3 (d), 128.7 (d), 130.3 (d), 131.2 (s), 146.3 (s), 152.9 (s), 158.2 ppm (s). Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.44; N, 6.89. Found: C, 70.81; H, 6.42; N, 6.86.

3-Isoamyl-1,4-benzoxazin-2-one (1c): bp 130 °C (2 mmHg); mp 28 °C; UV (EtOH) 210 (ϵ 13 800), 285 nm (9000); IR (KBr) 1725, 1615, 1200, 1078, 1020, 770 cm^{-1}; ^{1}H NMR δ 0.98 (d, 6 H, J = 7.3 Hz), 1.51–1.87 (m, 3 H), 2.76–2.97 (m, 2 H), 7.19–7.55 (m, 3 H), 7.66–7.76 (m, 1 H); ^{13}C NMR 22.3 (2 × q), 27.9 (d), 32.2 (t), 35.1 (t), 116.2 (d), 125.2 (d), 128.6 (d), 129.0 (d), 131.1 (s), 146.2 (s), 152.8 (s), 158.3 ppm (s). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.95; N, 6.44. Found: C, 71.74; H, 6.97; N, 6.38.

3-Phenyl-1,4-benzoxazin-2-one (1d): mp 116–117 °C (lit.[14] mp 117 °C); UV (EtOH) 210 (ϵ 25 000), 233 (8800), 327 nm (13 000); IR (KBr) 1745, 1735, 1605, 1125, 975, 765, 695 cm^{-1}; ^{1}H NMR δ 7.23–7.56 (m, 6 H), 7.70–7.89 (m, 1 H), 8.26–8.37 (m, 2 H); ^{13}C NMR 116.1 (d), 125.5 (d), 128.3 (2 × d), 129.3 (2 × d), 131.3 (d), 131.5 (s), 134.0 (s), 146.4 (s), 150.7 (s), 152.1 ppm (s).

General Procedure for the Photochemical Reactions of the 1,4-Benzoxazin-2-ones 1a–d in the Presence of Electron-Poor Olefins 2a–e. A solution of the 1,4-benzoxazin-2-one **1** (200 mg) in benzene (50 mL) in the presence of an excess of electron-poor olefin **2** (ca. 1 mL) in a Pyrex vessel under nitrogen was irradiated with a high-pressure mercury lamp (300 W) for 3–15 h at room temperature. After removal of the solvent, the residue was chromatographed on a silica gel (Wakogel D-300, flash chromatography) column with benzene–ethyl acetate (19:1–9:1) as eluent to give the corresponding (2 + 2) photocycloadducts **3–11′**.

Photocycloadduct 3: mp 106–107 °C; IR (KBr) 2230, 1755, 1490, 1278, 1125, 760, 743 cm^{-1}; ^{1}H NMR δ 1.49 (s, 3 H), 1.67 (s, 3 H), 2.94 (d, 1 H, J = 12.2 Hz), 3.15 (d, 1 H, J = 12.2 Hz), 6.97–7.22 (m, 4 H); ^{13}C NMR 21.8 (q), 25.8 (q), 43.8 (t), 56.8 (s), 60.8 (s), 117.4 (d), 121.0 (s), 123.4 (d), 125.2 (s), 125.6 (d), 126.0 (d), 146.7 (s), 168.3 ppm (s). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.31; H, 5.29: N, 12.24.

Photocycloadduct 3′: mp 101.5–102.5 °C; IR (KBr) 2230, 1765, 1490, 1275, 1125, 1105, 760 cm^{-1}; ^{1}H NMR δ 1.59 (s, 3 H), 1.79 (s, 3 H), 2.59 (d, 1 H, J = 12.2 Hz), 3.29 (d, 1 H, J = 12.2 Hz), 6.89–7.17 (m, 4 H); ^{13}C NMR 26.1 (q), 28.0 (q), 43.7 (t), 60.6 (s), 60.9 (s), 117.8 (d), 118.5 (s), 123.5 (d), 125.3 (d), 126.8 (d), 126.8 (s), 147.0 (s), 167.9 ppm (s). Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.30; H, 5.31; N, 12.31.

Photocycloadduct 4: mp 117–118 °C; IR (KBr) 1770, 1735, 1495, 1282, 1200, 1165, 1130, 1115, 758 cm^{-1}; ^{1}H NMR δ 1.34 (s, 3 H), 1.59 (s, 3 H), 2.79 (d, 1 H, J = 12.2 Hz), 3.00 (d, 1 H, J = 12.2 Hz), 3.85 (s, 3 H), 6.98–7.23 (m, 4 H); ^{13}C NMR 20.5 (q), 26.0 (q), 42.0 (t), 52.5 (q), 59.0 (s), 67.0 (s), 117.0 (d), 123.8 (d), 124.7 (d), 125.0 (d), 127.0 (s), 146.6 (s), 169.3 (s), 174.0 ppm (s). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.78; N, 5.36. Found: C, 64.40; H, 5.80; N, 5.33.

Photocycloadduct 4′: bp 125 °C (2 mmHg); IR (film) 1770, 1740, 1495, 1277, 1205, 1105, 755 cm^{-1}; ^{1}H NMR δ 1.59 (s, 3 H), 1.73 (s, 3 H), 2.40 (d, 1 H, J = 11.7 Hz), 3.24 (d, 1 H, J = 11.7 Hz), 3.42 (s, 3 H), 6.69–7.07 (m, 4 H); ^{13}C NMR 25.8 (q), 26.9 (q), 41.8 (t), 51.6 (q), 60.0 (s), 69.7 (s), 116.8 (d), 120.9 (d), 124.1 (d), 124.5 (d), 128.6 (s), 145.8 (s), 167.7 (s), 171.6 ppm (s). Anal. Calcd for $C_{14}H_{15}NO_4$: C, 64.35; H, 5.78; N, 5.36. Found: C, 64.54; H, 5.80; N, 5.41.

Photocycloadduct 5: mp 96.5–97.5 °C; IR (KBr) 2230, 1763, 1495, 1275, 1205, 1135, 1105, 772, 758 cm^{-1}; ^{1}H NMR δ 1.66 (s, 3 H), 3.07 (AB of ABX pattern, 2 H, J = 8.3, 8.3 Hz), 4.47 (X of ABX pattern, 1 H, J = 8.3, 8.3 Hz), 6.97–7.19 (m, 4 H); ^{13}C NMR 25.9 (q), 36.6 (t), 50.5 (d), 63.1 (s), 117.5 (d), 118.2 (s), 123.1 (d), 125.8 (d), 126.6 (d), 129.0 (s), 145.7 (s), 167.8 ppm (s). Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.70; N, 13.07. Found: C, 67.11; H, 4.72; N, 13.05.

Photocycloadduct 5′: mp 116.0–116.5 °C; IR (KBr) 2230, 1760, 1490, 1270, 1203, 1135, 1100, 1080, 765 cm^{-1}; ^{1}H NMR δ 1.61 (s, 3 H), 3.06 (AB of ABX pattern, 2 H, J = 3.9, 7.8 Hz), 4.74 (X of ABX pattern, 1 H, J = 3.9, 7.8 Hz), 6.89–7.22 (m, 4 H); ^{13}C NMR 25.7 (q), 35.9 (t), 51.6 (d), 64.1 (s), 116.3 (s), 117.4 (d), 123.1 (d), 125.5 (s), 125.5 (d), 126.5 (d), 146.9 (s), 167.6 ppm (s). Anal. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.70; N, 13.07. Found: C, 67.21; H, 4.71; N, 13.09.

Photocycloadducts 6 and **6′** were not completely separated. Their structures were elucidated on the basis of NMR spectra of mixtures of them. **6**: ^{1}H NMR δ 1.60 (s, 3 H), 2.91 (AB of ABX pattern, 2 H, J = 7.8, 8.8 Hz), 3.83 (s, 3 H), 4.30 (X of ABX pattern, 1 H, J = 7.8, 8.8 Hz), 6.74–7.74 (m, 4 H); ^{13}C NMR 21.3 (q), 35.5 (t), 52.4 (q), 61.2 (s), 62.8 (d), 168.8 (s), 171.6 ppm (s) in addition to aromatic carbon peaks. **6′**: ^{1}H NMR δ 1.57 (s, 3 H), 2.88 (AB of ABX pattern, 2 H, J = 3.9, 7.8 Hz), 3.50 (s, 3 H), 4.61 (X of ABX pattern, 1 H, J = 3.9, 7.8 Hz), 6.74–7.74 (m, 4 H); ^{13}C NMR 26.1 (q), 34.6 (t), 52.0 (q), 63.5 (d), 63.8 (s), 167.5 (s), 171.2 ppm (s) in addition to aromatic carbon peaks. Anal (for a mixture of **6** and **6′**). Calcd for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.29; N, 5.66. Found C, 63.11; H, 5.47; N, 5.28.

Photocycloadduct 7: mp 133–134 °C; IR (KBr) 1760, 1742, 1645, 1495, 1270, 1170, 1180, 770, 760 cm^{-1}; ^{1}H NMR δ 1.60 (s, 3 H), 2.95 (AB of ABX pattern, 2 H, J = 3.9, 7.8 Hz), 4.54 (dd,

---

[11] Irradiation of 3-methyl-1,4-benzoxazin-2-one (**1a**) in the presence of amines such as triethylamine, diethylamine, and propylamine gave the reductive dimers (*dl*- and *meso*-**12a**) via electron transfer mechanism: Nishio, T.; Omote, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 1293.

[12] Corey, E. J.; Bass, J. D.; LeMahieu, R.; Mitra, R. B. *J. Am. Chem. Soc.* **1964**, *86*, 5570.

[13] Biekert, E.; Hoffmann, D.; Meyer, F. J. *Chem. Ber.* **1961**, *94*, 1664.

[14] Mofett, R. B. *J. Med. Chem.* **1966**, *9*, 475.

1 H, J = 2.0, 13.7 Hz), 4.67 (X of ABX pattern, 1 H, J = 3.9, 7.8 Hz), 4.85 (dd, 1 H, J = 2.0, 13.7 Hz), 6.76–7.10 (m, 5 H); ^{13}C NMR 26.1 (q), 34.6 (t), 63.2 (d), 63.9 (s), 99.3 (t), 117.2 (d), 120.9 (d), 124.5 (d), 124.9 (d), 128.3 (s), 140.1 (d), 146.5 (s), 167.4 (s), 167.8 ppm (s). Anal. Calcd for $C_{14}H_{13}NO_4$: C, 64.85; H, 5.05; N, 5.40. Found: C, 64.59; H, 5.02; N, 5.34.

Photocycloadduct 8: mp 71.5–72.0 °C; IR (KBr) 2220, 1760, 1495, 1278, 1220, 758 cm^{-1}; ^{1}H NMR δ 0.83 (t, 3 H), 1.1–1.6 (m, 4 H), 1.78 (s, 3 H), 1.7–2.0 (m, 2 H), 2.62 (d, 1 H, J = 12.2 Hz), 3.21 (d, 1 H, J = 12.2 Hz), 6.89–7.26 (m, 4 H); ^{13}C NMR 13.6 (q), 22.4 (t), 25.0 (t), 27.8 (q), 39.3 (t), 42.0 (t), 60.8 (s), 63.8 (s), 117.5 (d), 118.7 (s), 122.9 (d), 125.2 (d), 126.6 (d), 127.6 (s), 146.8 (s), 167.6 ppm (s). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.08; H, 6.71; N, 10.36. Found: C, 71.05; H, 6.72; N, 10.40.

Photocycloadduct 9: bp 145 °C (2 mmHg); IR (film) 1760, 1740, 1490, 1275, 1200, 1160, 1135, 1125, 750 cm^{-1}; ^{1}H NMR δ 0.85 (t, 3 H), 1.19–1.48 (m, 4 H), 1.72 (s, 3 H), 1.72–2.0 (m, 2 H), 2.35 (d, 1 H, J = 12.2 Hz), 3.18 (d, 1 H, J = 12.2 Hz), 3.42 (s, 3 H), 6.17–6.99 (m, 4 H); ^{13}C NMR 13.6 (q), 22.5 (t), 25.0 (t), 25.6 (q), 40.1 (t), 40.6 (t), 51.6 (q), 63.2 (s), 69.8 (s), 116.7 (d), 120.6 (d), 124.0 (d), 124.5 (d), 129.6 (s), 146.0 (s), 167.6 (s), 171.7 ppm (s). Anal. Calcd for $C_{17}H_{21}NO_4$: C, 67.30; H, 6.92; N, 4.61. Found: C, 67.42; H, 6.94; N, 4.67.

Photocycloadduct 10: bp 135 °C (2 mmHg); IR ($CHCl_3$) 2220, 1750, 1485, 1315, 1270, 1138 cm^{-1}; ^{1}H NMR δ 0.85 (d, 6 H, J = 5.9 Hz), 1.48 (s, 3 H), 0.94–2.02 (m, 5 H), 2.85 (d, 1 H, J = 12.2 Hz), 3.14 (d, 1 H, J = 12.2 Hz), 6.95–7.39 (m, 4 H); ^{13}C NMR 22.3 (2 × q), 27.9 (d), 31.8 (t), 37.7 (t), 42.2 (t), 56.7 (s), 64.0 (s), 117.4 (d), 121.0 (s), 123.1 (d), 125.5 (d), 125.9 (d), 130.3 (s), 146.7 (s), 168.1 ppm (s). Anal. Calcd for $C_{17}H_{20}N_2O_2$: C, 71.80; H, 7.08; N, 9.85. Found: C, 71.77; H, 7.15; N, 9.50.

Photocycloadduct 10′: mp 101–101.5 °C; IR (KBr) 2225, 1762, 1490, 1275, 1140, 1085, 758 cm^{-1}; ^{1}H NMR δ 0.82 (d, 6 H, J = 6.4 Hz), 1.79 (s, 3 H), 1.06–1.97 (m, 5 H), 2.61 (d, 1 H, J = 12.2 Hz), 3.22 (d, 1 H, J = 12.2 Hz), 6.89–7.27 (m, 4 H); ^{13}C NMR 22.3 (2 × q), 27.9 (q), 27.9 (d), 31.6 (t), 37.9 (t), 42.0 (t), 60.8 (s), 63.8 (s), 117.7 (d), 118.7 (s), 123.0 (d), 125.3 (d), 126.6 (d), 127.6 (s), 146.9 (s), 167.7 ppm (s). Anal. Calcd for $C_{17}H_{20}N_2O_2$: C, 71.80; H, 7.08; N, 9.85. Found: C, 71.67; H, 7.09; N, 9.79.

Photocycloadduct 11: bp 135 °C (2 mmHg); IR (film) 1760, 1740, 1485, 1310, 1270, 1200, 1120, 750 cm^{-1}; ^{1}H NMR δ 0.81 (d, 3 H, J = 6.3 Hz), 0.83 (d, 3 H, J = 6.3 Hz), 1.34 (s, 3 H), 1.01–1.97 (m, 5 H), 2.72 (d, 1 H, J = 12.2 Hz), 3.01 (d, 1 H, J = 12.2 Hz), 3.85 (s, 3 H), 6.91–7.41 (m, 4 H); ^{13}C NMR 20.8 (q), 22.3 (2 × q), 28.0 (d), 31.9 (t), 40.6 (t), 52.5 (q), 62.2 (s), 66.8 (s), 116.8 (d), 123.5 (d), 124.5 (d), 124.9 (d), 127.9 (s), 146.6 (s), 169.0 (s), 174.0 ppm (s). Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.11 ; H, 7.30; N, 4.41. Found: C, 68.42; H, 7.49; N, 4.49.

Photocycloadduct 11′: bp 130 °C (2 mmHg); IR (film) 1763, 1740, 1495, 1320, 1275, 1205, 1160, 1130, 750 cm^{-1}; ^{1}H NMR δ 0.85 (d, 6 H, J = 5.4 Hz), 1.18–1.56 (m, 3 H), 1.71 (s, 3 H), 1.78–1.97 (m, 2 H), 2.39 (d, 1 H, J = 12.2 Hz), 3.17 (d, 1 H, J = 12.2 Hz), 3.41 (s, 3 H), 6.70–7.00 (m, 4 H); ^{13}C NMR 22.4 (2 × q), 25.8 (q), 28.1 (d), 31.8 (t), 38.9 (t), 40.2 (t), 51.8 (q), 63.4 (s), 69.9 (s), 116.9 (d), 120.8 (d), 124.1 (d), 124.3 (d), 129.7 (s), 146.1 (s), 167.7 (s), 171.8 ppm (s). Anal. Calcd for $C_{18}H_{23}NO_4$: C, 68.11; H, 7.30; N, 4.41. Found: C, 68.33; H, 7.37; N, 4.47.

Reductive dimer *dl*-12a: mp 196–197 °C; IR (KBr) 3390, 1740, 1725, 1615, 1500, 1305, 1225, 1065, 740 cm^{-1}; ^{1}H NMR ($CDCl_3$–Me_2SO-d_6) δ 1.58 (s, 6 H), 6.40 (br s, 2 H), 6.53–6.97 (m, 8 H); ^{13}C NMR ($CDCl_3$–Me_2SO-d_6) 21.9 (2 × q), 63.9 (2 × s), 114.3 (2 × d), 115.4 (2 × d), 117.6 (2 × d), 124.6 (2 × d), 131.1 (2 × s), 139.1 (2 × s), 166.6 ppm (2 × s); (chemical ionization mass spectrum, m/e 325 (QM$^+$). Anal. Calcd for $C_{18}H_{16}N_2O_4$: C, 66.65; H, 4.97; N, 8.63. Found: C, 66.73; H, 5.00; N, 8.62.

In the ^{1}H NMR spectra of **12a** the methyl protons (δ 1.58) appear at higher field than those (δ 1.66)[11] in *meso*-**12a**, probably due to the shielding effect of the aromatic ring, so we assume that **12a** thus obtained here might be the *dl* isomer.

Reductive dimer *dl*- or *meso*-12b: mp 128.5–129 °C; IR (KBr) 3370, 1730, 1620, 1500, 1305, 1203, 738 cm^{-1}; ^{1}H NMR δ 0.71 (d, 12 H, J = 4.9 Hz), 0.95–1.70 (m, 8 H), 2.10–2.58 (m, 2 H), 5.06 (s, 2 H), 6.63–7.08 (m, 8 H); ^{13}C NMR 22.3 (2 × q), 28.1 (2 × d), 33.1 (2 × t), 34.5 (2 × t), 68.8 (2 × s), 113.6 (2 × d), 116.1 (2 × d), 118.7 (2 × d), 125.8 (2 × d), 131.3 (2 × s), 138.7 (2 × s), 166.8 ppm (2 × s). Anal. Calcd for $C_{26}H_{32}N_2O_4$: C, 71.53; H, 7.38; N, 6.41. Found: C, 71.43; H, 7.39; N, 6.34.

One stereoisomer (*dl*- or *meso*-**12b**) was predominantly formed under these experimental conditions; however, the stereochemistry of **12b** is uncertain at present.

Registry No. **1a**, 7653-60-3; **1b**, 95483-38-8; **1c**, 95483-39-9; **1d**, 27990-57-4; **2a**, 126-98-7; **2b**, 80-62-6; **2c**, 107-13-1; **2d**, 96-33-3; **2e**, 2177-18-6; **3**, 95483-40-2; **3′**, 95483-41-3; **4**, 95483-42-4; **4′**, 95483-43-5; **5**, 95483-44-6; **5′**, 95483-45-7; **6**, 95483-46-8; **6′**, 95483-47-9; **7**, 95483-48-0; **8**, 95483-49-1; **9**, 95483-50-4; **10**, 95483-51-5; **10′**, 95483-52-6; **11**, 95483-53-7; **11′**, 95483-54-8; *dl*-**12a**, 95587-00-1; **12b**, 95483-55-9.

Metallic Nickel-Mediated Synthesis of Ketones by the Reaction of Benzylic, Allylic, Vinylic, and Pentafluorophenyl Halides with Acid Halides

Shin-ichi Inaba and Reuben D. Rieke*

Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588-0304

Received July 3, 1984

Metallic nickel was investigated as a convenient coupling reagent for the synthesis of ketones by the reaction of benzylic, allylic, vinylic, and pentafluorophenyl halides with acid halides at 85 °C in glyme. A variety of benzylic ketones with functional groups including halogen, cyano, methoxycarbonyl, and hydroxycarbonyl groups were prepared in good yields by this method. The reaction was demonstrated to proceed via organonickel halide intermediates formed by the smooth oxidative addition of benzylic and acyl halides to metallic nickel, which were trapped with electron-deficient olefins. (π-Allyl)nickel halides, prepared in situ at 85 °C from allylic halides and the nickel, also worked for the preparation of ketones. Vinylic and pentafluorophenyl halides but not alkyl halides reacted with acid halides to give the corresponding ketones in moderate yields.

The reaction of organometallic reagents with acid halides is one of the more useful methods for the synthesis of ketones. A variety of organometallic reagents has been employed for this purpose, each of which displays varying degrees of success in avoiding the side reaction of further reaction of the reagents with the ketones formed. For example, organomagnesium,[1,2] -zinc,[1,3] -cadmium,[1] -mercury,[4] -boron,[5] -aluminum,[6,7] -silicon,[8] -copper,[9–11] -zirconium,[12] -manganese,[13] and -rhodium[14] compounds have all

---

(1) Shirley, D. A. *Org. React. (N.Y.)* **1954**, *8*, 28.

(2) At low temperature: Sato, F.; Inoue, M.; Ogura, K.; Sato, M. *Tetrahedron Lett.* **1979**, 4303. Eberle, M. K.; Kahle, G. G. *Tetrahedron Lett.* **1980**, *21*, 2303. In HMPA: Fauvarque, J.; Ducom, J.; Fauvarque, J. F. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1972**, *275*, 511. In the presence of a catalytic amount of transition-metal halide, for example: Cook, N. C.; Percival, W. C. *J. Am. Chem. Soc.* **1949**, *71*, 4141. Cason, J.; Kraus, K. W. *J. Org. Chem.* **1961**, *26*, 1772.

0022-3263/85/1950-1373$01.50/0