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Photochemical [2+2] Cycloreversion Reactions of 1,2,2a,8b-Tetrahydrocyclobuta[*c*]isoquinolin-4(3*H*)-ones[1)]

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Irradiation (350 nm) of 2-(3-butenyl)- and 2-(4-pentenyl)isoquinolin-1(2*H*)-ones (**1a** and **1b**) afforded the intramolecular [2+2] adducts (**2a** and **2b**). The additions proceeded regioselectively to give only the parallel adducts. Though stable to irradiation at 350 nm, these adducts (**2a** and **2b**) gave *o*-vinylbenzamide derivatives (**3a** and **3b**) on irradiation at 300 nm. The intermolecular [2+2] adducts (**7d** and **7e**) obtained by irradiation ($\geq$300 nm) of isoquinolin-1(2*H*)-one (**6**) in the presence of a large excess of alkenes were also found to be unstable and reverted to the original components [isoquinolin-1(2*H*)-one (**6**) and alkenes] on irradiation at 300 nm in the absence of the alkenes.

Keywords——2-(ω-alkenyl)isoquinolin-1(2*H*)-one; photochemical [2+2] cycloaddition; photochemical [2+2] cycloreversion; olefin metathesis; photo–photo olefin metathesis; *o*-vinylbenzamide derivative; wavelength dependency

Photochemical cycloaddition of isoquinolin-1(2*H*)-one and its derivatives to olefins, affording intermolecular [2+2] adducts, is known to proceed on irradiation of the former at $\geq$300 nm in the presence of a large excess of the latter.[2,3)] Here, we report that these adducts as well as the intramolecular [2+2] adducts obtained from 2-(ω-alkenyl)isoquinolin-1(2*H*)-ones by irradiation at 350 nm, are unstable to irradiation at 300 nm and either revert to the original components or afford *o*-vinylbenzamide derivatives. The two modes of photochemical [2+2] cycloreversion reactions are dependent upon the structure of the adducts. That is, the intramolecular adducts derived from 2-(3-butenyl)- or 2-(4-pentenyl)isoquinolin-1(2*H*)-ones afford *o*-vinylbenzamide derivatives, while the intermolecular adducts always revert to the original components [isoquinolin-1(2*H*)-one and alkenes]. The former mode of the photochemical cycloreversion reaction, if combined with the first intramolecular photoaddition reaction, provides a novel photo–photo olefin metathesis[4,5)] giving *o*-vinylbenzamide derivatives from 2-(ω-alkenyl)isoquinolin-1(2*H*)-ones.

Irradiation of 2-(3-butenyl)isoquinolin-1(2*H*)-one (**1a**) in methanol at 350 nm until almost all of the starting material had been consumed afforded the adduct (**2a**) as a sole product in 73% yield. Longer irradiation under these conditions, however, resulted in slow consumption of **2a** with the formation of a new product (**3a**). Though the formation of **3a** from **2a** was very slow under these conditions, irradiation of **2a** at 300 nm rapidly and irreversibly gave **3a** again as a sole product in 72% yield. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of **3a** clearly revealed the presence of a vinyl group attached to the benzene ring [δ ($CDCl_3$): 5.23 (dd, J=10 and 1.3 Hz), 5.53 (dd, J=18 and 1.3 Hz), and 6.70 (dd, J=10 and 18 Hz)]. This fact as well as the reductive transformation of **3a** to 1-(2-ethylbenzyl)pyrrolidine (**5**) *via* 1-(2-ethylbenzoyl)pyrrolidine (**4**) pointed to an *o*-vinylbenzamide structure (**3a**) and excluded the other possible structure (**3'a**). Once the structure of **3a** was determined, the initially formed [2+2] adduct was also determined as **2a** (a

parallel addition product) and not as **2a'** (a cross addition product). The entire sequence from **1a** to **3a** *via* **2a** corresponds to a new type of photo–photo olefin metathesis. In the same manner, 2-(4-pentenyl)isoquinolin-1(2*H*)-one (**1b**) was also converted to **3b** [$\delta(CDCl_3)$: 5.25 (dd, $J=10$ and 1.3 Hz), 5.65 (dd, $J=18$ and 1.3 Hz), and 6.70 (dd, $J=18$ and 10 Hz)] in a satisfactory overall yield. Here, again, the initial photoaddition reaction proceeds regioselectively to give only the parallel adduct (**2b**). Since both reactions (**1**→**2** and **2**→**3**) proceed smoothly on irradiation at ≥300 nm, the synthesis of *o*-vinylbenzamide derivatives (**3**) can easily be carried out without the isolation of **2** on a preparative scale by using a high-pressure mercury arc lamp with a Pyrex filter.

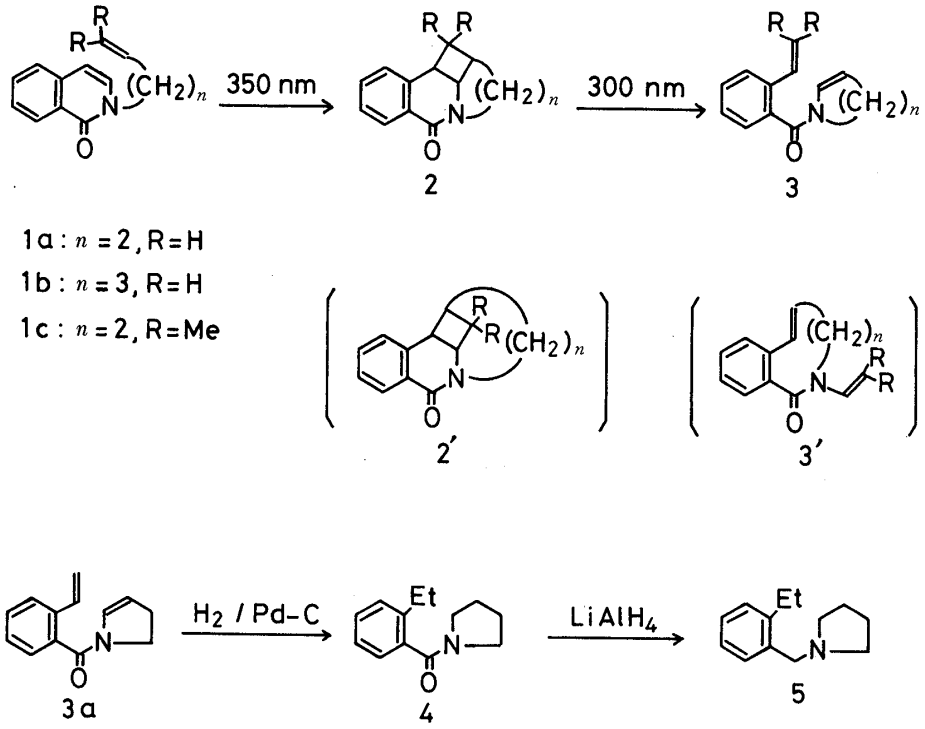

Chart 1

Photo-instability of the intramolecular adducts (**2a** and **2b**)[6] under irradiation at 300 nm prompted us to examine the photoreaction of the intermolecular adducts obtained by the photoaddition of isoquinolin-1(2*H*)-one (**6**) to olefins. Evanega and Fabiny[2] reported a regioselective formation of 1,1-dimethyl-1,2,2a,8b-tetrahydrocyclobuta[*c*]isoquinolin-4(3*H*)-one (**7d**) by irradiation (350 nm) of **6** in the presence of a large excess of isobutene. Though we obtained the same adduct (**7d**) as the major product, a new product (**8**) was also obtained in a small amount.[7] As reported already,[8] this type of intermolecular photoaddition is assumed to proceed in a stepwise manner *via* the biradical intermediate (A). Intermediacy of A not only accounts for the regioselectivity of the photoaddition giving **7d**, but also explains the formation of the by-product (**8**: an ene-type reaction product) as shown by the arrow symbols in the formula A. The adduct (**7d**) was then irradiated in methanol at 300 nm to give **6** (55%) and a trace of **8** (detected by thin-layer chromatography: TLC), and no **9** (a presumed metathetical product) was detected in the reaction mixture. These experiments indicate that the C^1–C^{8b} bond in **7d** is cleaved by irradiation at 300 nm (but not at 350 nm) to give the radical (A), whose major fate is either reversion to **6** or recyclization to **7d**. In the absence of an excess of isobutene, **7d** would finally be consumed under irradiation at 300 nm, because A can no longer be formed from **6**. However, as is evident from its formation from **6** by irradiation at ≥300 nm,[2] **7d** is the major product of the photolysis in the presence of an excess

of isobutene. In this photolysis, the ene-type product (**8**) is also obtained, though in a small amount. Though the formation of **8** from the radical (A) is a minor path, the reformation of A from **7d** by irradiation at ≥ 300 nm should accumulate **8** in an amount sufficient for its isolation. Such a cycloreversion reaction to **6** was also observed in the irradiation of 1,2,2a,8b-tetrahydrocyclobuta[*c*]isoquinolin-4(3*H*)-one (**7e**)[9] at 300 nm. Hence, photocycloreversion of these intermolecular adducts (**7**) to **6** (or more strictly speaking, A) is a common phenomenon and does not depend upon the substituent at the 1-position of **7**.

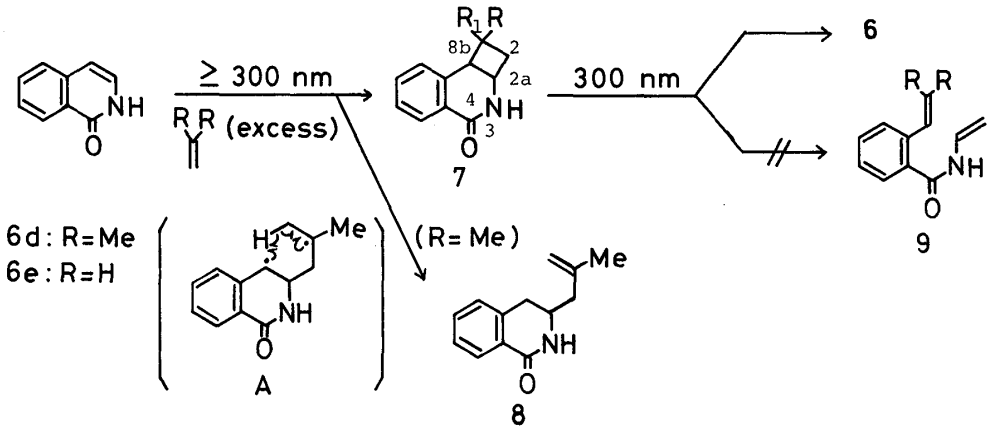

Chart 2

In order to clarify the mechanism of the formation of *o*-vinylbenzamide derivatives from the intramolecular photoadducts (**2**), we then irradiated 2-(4-methyl-3-pentenyl)isoquinolin-1(2*H*)-one (**1c**) at 350 nm. Again, the parallel adduct (**2c**) and the ene-type product (**10**) were obtained in yields of 74 and 3%, respectively. The adduct (**2c**) was then irradiated at 300 nm to give **3c** and **10** with recovery of **2c** in yields of 21, 6, and 19%, respectively. Longer irradiation under these conditions did not cause any change of the ratio of **3c** and **10** (*ca.* 3.5 : 1). The difference between these two irradiation experiments can be explained in the following way. First, two radicals (A′ and B′) would be formed by irradiation of **2c** at 300 nm. The former

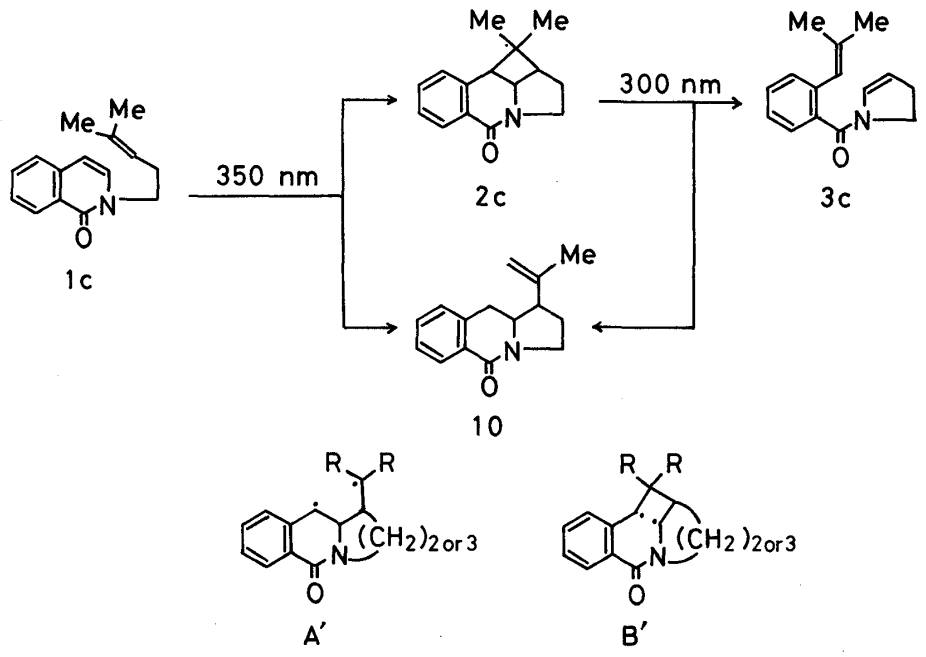

Chart 3

radical (A′) also would be formed from **1c** by irradiation at 350 nm. The radical A′ then cyclizes mostly to **2c** and partly to **10**, as is evident from the result of the irradiation experiment on **1c** at 350 nm (the ratio of **2c** and **10** was *ca.* 25 : 1). An increased ratio of **3c** and **10** (*ca.* 3.5 : 1) in the photolysis of **2c** at 300 nm indicates that both radicals (A′ and B′) are formed from **2c**. Then, it is reasonable to assume that the radical B′ would be transformed solely to the *o*-vinylbenzamide derivative (**3c**). While detailed data are lacking at present, this mechanism can account for the above experimental results at least in a qualitative manner. Further study to confirm the validity of this mechanism is in progress.

The absence of formation of **9** from **7** indicates that the radical corresponding to B′ is not formed from **7**, and this suggests that the presence of a methylene bridge ($n=2$ or 3) between C^2 and N^3 in **2** is essential for the formation of B′.[10]

While mechanistic details of the second step in this novel photo–photo metathesis are not clear at present, the method provides a convenient route[11] to *o*-vinylbenzamide derivatives from 1-isoquinolone which is readily applicable on a preparative scale. Furthermore, this photo–photo metathesis might provide a new and simple route to lycorine-type alkaloids by the use of 2-(alkadienyl)isoquinolin-1(2*H*)-ones (*e.g.*, **11** and **12**)[12] as starting materials.

Further studies along this line are in progress.

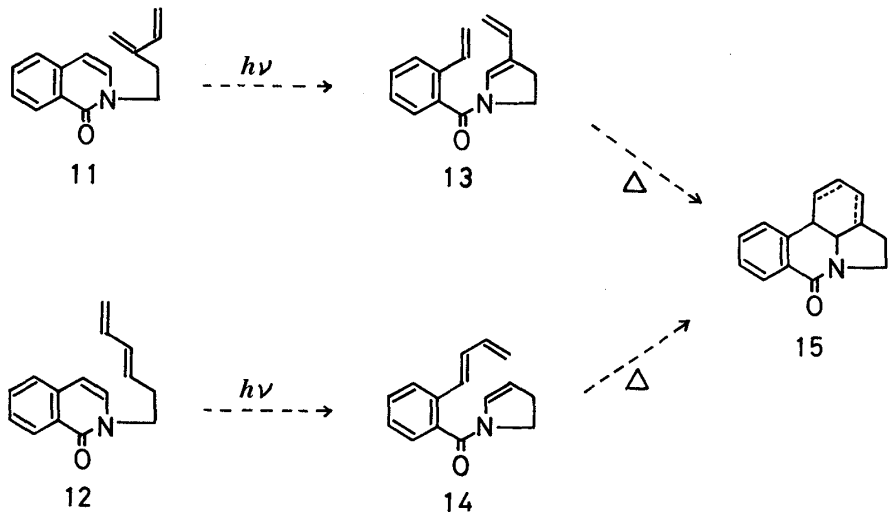

Chart 4

Experimental

All melting points were determined on a micro-hot stage (Yanagimoto) and are uncorrected. Infrared (IR) spectra were recorded on a JASCO A-102 spectrometer, ultraviolet (UV) spectra with a Hitachi 320 spectrometer, and ^{1}H-NMR spectra on a JEOL JNM-PMX 60 or JNM-FX-100 spectrometer (with tetramethylsilane as an internal standard). Mass spectra (MS) were taken with a JEOL JNM-01SG spectrometer. Column chromatography was performed on silica gel (Wakogel C-200) and TLC on Merck Kieselgel 60F 254.

Irradiation Conditions——a) Irradiation at ≥300 nm: The photolyses were carried out in a Pyrex immersion apparatus equipped with an Ushio 450W high-pressure mercury lamp.

b) Irradiation at 300 nm or 350 nm: Irradiation for the photochemical reactions having a wavelength dependency was performed in a quartz vessel using Rayonet photochemical reactor lamps (RPR-3000 Å or RPR-3500 Å) under an argon atmosphere.

Photochemical Cycloaddition of Isoquinolin-1(2*H*)-one (6) to Isobutene or Ethylene——A solution of **6** (435 mg, 3 mmol) in MeOH (150 ml) was irradiated at ≥300 nm under bubbling of isobutene for 8 h. After evaporation of the solvent, the residue was chromatographed on silica gel (40 g). Elution with hexane–ether (1 : 1) afforded first 8 mg (1%) of the ene-product (**8**), then 115 mg (19%) of the [2+2] adduct [**7d**, mp 151—160 °C (acetone)],[2] and finally 123 mg (28%) of the recovered starting material (**6**). Elution with CH_2Cl_2–MeOH (19 : 1) gave 87 mg (20%) of the photodimer of isoquinolin-1-(2*H*)-one, mp 301—302 °C [AcOH–EtOH–H_2O (10 : 5 : 1)].[2]

3-(2-Methyl-2-propenyl)-3,4-dihydroisoquinolin-1(2*H*)-one (**8**), mp 154—156 °C (acetone). *Anal.* Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.48; H, 7.68; N, 6.68. UV λ_{max}^{MeOH} nm: 205, 233, 276 (sh). IR (KBr): 3410, 1660 cm^{-1}. NMR ($CDCl_3$) δ: 1.80 (3H, s), 2.35 (2H, d, J=7 Hz), 2.90 (2H, d, J=6 Hz), 3.60—4.05 (1H, m), 4.85—5.05 (2H, m), 5.84 (1H, br s), 7.2—7.55 (3H, m), 8.0—8.2 (1H, m).

1,2,2a,8b-Tetrahydrocyclobuta[*c*]isoquinolin-4(3*H*)-one (**7e**) was obtained in *ca.* 30% yield by photoaddition of **6** to ethylene under conditions similar to those described above, except for the use of aceton–methanol (2 : 3) as the solvent.

7e, mp 122—124 °C (CH_3COOEt–hexane). *Anal.* Calcd for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.21; H, 6.21; N, 8.00. UV λ_{max}^{MeOH} nm: 206, 255 (sh), 260 (sh), 280 (sh). IR ($CHCl_3$): 3420, 1663 cm^{-1}. NMR ($CDCl_3$) δ: 1.9—2.65 (4H, m), 3.6—4.0 (1H, m), 4.0—4.5 (1H, m), 7.05—7.65 (4H, m), 8.1—8.3 (1H, m).

Photochemical Cycloreversion of 1,2,2a,8b-Tetrahydrocyclobuta[*c*]isoquinolin-4(3*H*)-one (7e) or Its 1,1-Dimethyl Derivative (7d) to Isoquinolin-1(2*H*)-one (6)——A solution of **7d** (30 mg, 0.15 mmol) in MeOH (25 ml) was irradiated at 300 nm for 1.5 h under an argon atmosphere. The residue obtained after evaporation of the solvent was chromatographed on silica gel (5 g) to give 12 mg (55%) of **6**.

Under the same irradiation conditions, a 51% yield of **6** was obtained from **7e**.

Synthesis of 2-(ω-Alkenyl)isoquinolin-1(2*H*)-ones (1a—c)——Synthesis of 2-(3-butenyl)isoquinolin-1(2*H*)-one (**1a**) as a Typical Example: Finely powdered KOH (5.6 g, 0.1 mol) and $(n\text{-}Bu)_4N^+HSO_4^-$ (1.36 g, 4 mmol) were added to a solution of **6** (1.45 g, 10 mmol) in benzene (200 ml). Under stirring, 4-bromo-1-butene (6.75 g, 50 mmol) was added to the above solution and the whole was refluxed for 1 h. After evaporation of the solvent, the residue was taken up in CH_2Cl_2. The organic layer was washed with 5% aq. NaOH and then with 5% HCl and dried over Na_2SO_4. The residue obtained after evaporation of the solvent was chromatographed on silica gel (80 g). Elution with hexane–CH_2Cl_2 (1 : 1) gave 40 mg (2%) of 1-(3-butenyloxy)isoquinoline. Elution with CH_2Cl_2 gave 1.59 g (80%) of **1a**.

1a. Colorless oil. High-resolution MS *m/z*: M^+ Calcd for $C_{13}H_{13}NO$: 199.0996. Found: 199.1006. UV λ_{max}^{MeOH} nm (log ε): 206 (3.03), 221 (3.52, sh), 247 (3.78, sh), 278 (3.89), 286 (3.88), 312 (3.52, sh), 323 (3.58), 336 (3.42, sh). IR (KBr): 1645, 1623 cm^{-1}. NMR ($CDCl_3$) δ: 2.50 (2H, q, J=7 Hz), 3.98 (2H, t, J=7 Hz), 4.85—5.27 (2H, m), 5.47—6.07 (1H, m), 6.30 (1H, d, J=7 Hz), 6.98 (1H, d, J=7 Hz), 7.32—7.65 (3H, m), 8.23—8.47 (1H, m).

1-(3-Butenyloxy)isoquinoline. Colorless oil. High-resolution MS *m/z*: M^+ Calcd for $C_{13}H_{13}NO$: 199.0996. Found: 199.1005. UV λ_{max}^{MeOH} nm: 264 (sh), 273, 283, 311, 324. IR ($CHCl_3$): 1625 cm^{-1}. NMR (CCl_4) δ: 2.60 (2H, q, J=7 Hz), 4.53 (2H, t, J=7 Hz), 4.93—5.37 (2H, m), 5.62—6.33 (1H, m), 7.07 (1H, d, J=6 Hz), 7.30—7.70 (3H, m), 7.90 (1H, d, J=6 Hz), 8.07—8.33 (1H, m).

The following compounds were prepared in the same manner.

2-(4-Pentenyl)isoquinolin-1(2*H*)-one (**1b**). Yield: 82%. Colorless oil. High-resolution MS *m/z*: M^+ Calcd for $C_{14}H_{15}NO$: 213.1153. Found: 213.1155. IR ($CHCl_3$): 1643, 1623 cm^{-1}. NMR (CCl_4) δ: 1.60—2.35 (4H, m), 3.90 (2H, t, J=7 Hz), 4.80—5.20 (2H, m), 5.50—6.15 (1H, m), 6.30 (1H, d, J=7.5 Hz), 6.98 (1H, d, J=7.5 Hz), 7.25—7.60 (3H, m), 8.25—8.48 (1H, m).

1-(4-Pentenyloxy)isoquinoline. Yield: 3%. Colorless oil. High-resolution MS *m/z*: M^+ Calcd for $C_{14}H_{15}NO$: 213.1153. Found: 213.1191. IR ($CHCl_3$): 1623 cm^{-1}. NMR (CCl_4) δ: 1.75—2.52 (4H, m), 4.50 (2H, t, J=6.5 Hz), 4.85—5.27 (2H, m), 5.57—6.38 (1H, m), 7.10 (1H, d, J=6 Hz), 7.33—7.75 (3H, m), 7.90 (1H, d, J=6 Hz), 8.13—8.33 (1H, m).

2-(4-Methyl-3-pentenyl)isoquinolin-1(2*H*)-one (**1c**). Yield: 85%. Colorless oil. High-resolution MS *m/z*: M^+ Calcd for $C_{15}H_{17}NO$: 227.1309. Found: 227.1292. IR ($CHCl_3$): 1640, 1620 cm^{-1}. NMR (CCl_4) δ: 1.53 (3H, s), 1.63 (3H, s), 2.42 (2H, q, J=7 Hz), 3.90 (2H, t, J=7 Hz), 5.15 (1H, br t, J=7 Hz), 6.27 (1H, d, J=7.5 Hz), 6.97 (1H, d, J=7.5 Hz), 7.30—7.60 (3H, m), 8.28—8.48 (1H, m).

1-(4-Methyl-3-pentenyloxy)isoquinoline. Yield: 4%. Colorless oil. High-resolution MS *m/z*: M^+ Calcd for $C_{15}H_{17}NO$: 227.1309. Found: 227.1293. IR ($CHCl_3$): 1623 cm^{-1}. NMR (CCl_4) δ: 1.77 (6H, br s), 2.60 (2H, q, J=7 Hz), 4.50 (2H, t, J=7 Hz), 5.33 (1H, br t, J=7 Hz), 7.15 (1H, d, J=6 Hz), 7.40—7.80 (3H, m), 7.98 (1H, d, J=6 Hz), 8.17—8.32 (1H, m).

General Procedure for Irradiation of 2-(ω-Alkenyl)isoquinolin-1(2*H*)-ones (1) to the Parallel Adducts (2)——A solution of **1** (1 mmol) in MeOH (120 ml) was irradiated at 350 nm under an argon atmosphere for 30 min at room temperature. The solvent was evaporated off and the residue was recrystallized from ether–hexane or chromatographed on silica gel with ether–hexane (1 : 4, v/v) to afford the corresponding parallel adduct (**2**).

5-Oxo-1a,2,3,5,9b,9c-hexahydro-1*H*-cyclobuta[*hi*]benzo[*f*]indolizine (**2a**). Yield: 145 mg (73%). Colorless prisms, mp 96—98 °C (ether–hexane). *Anal.* Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.03; H, 6.60; N, 6.76. UV λ_{max}^{MeOH} nm (log ε): 256 (3.68), 265 (3.62 sh). IR ($CHCl_3$): 1635 cm^{-1}. NMR ($CDCl_3$) δ: 1.50—2.30 (3H, m), 2.50—3.30 (3H, m), 3.40 (1H, dt, J=5.5, 8.5 Hz), 4.20 (1H, dt, J=3.5, 5.5 Hz), 4.62 (1H, ddd, J=3, 9, 12 Hz), 6.90—7.50 (3H, m), 7.95—8.17 (1H, m).

6-Oxo-1a,3,4,6,10b,10c-hexahydro-1*H*,2*H*-cyclobuta[*ij*]benzo[*b*]quinolizine (**2b**). Yield: 150 mg (70%). Colorless prisms, mp 101—102 °C (ether–hexane). High-resolution MS *m/z*: M^+ Calcd for $C_{14}H_{15}NO$: 213.1153. Found: 213.1161. UV λ_{max}^{MeOH} nm: 202, 258, 267, 285 (sh). IR ($CHCl_3$): 1630 cm^{-1}. NMR ($CDCl_3$) δ: 1.20—2.90 (8H, m), 3.40

(1H, dt, J=5.5, 8.5 Hz), 4.18 (1H, dt, J=3.5, 5.5 Hz), 4.6—4.9 (1H, m), 6.9—7.5 (3H, m), 7.9—8.2 (1H, m).

1,1-Dimethyl-5-oxo-1a,2,3,5,9b,9c-hexahydro-1*H*-cyclobuta[*hi*]benzo[*f*]indolizine (2c) and 1-Isopropenyl-5-oxo-1,2,3,5,10,10a-hexahydropyrrolo[1,2-*b*]isoquinoline (10)——The residue obtained after evaporation of the solvent was chromatographed on silica gel with ether–hexane (1 : 3, v/v) to give first **2c** and then **10**.

The parallel adduct (**2c**). Yield: 169 mg (74%). Colorless prisms, mp 95—96 °C (ether–hexane). *Anal.* Calcd for $C_{15}H_{17}NO$: C, 79.26; H, 7.54; N, 6.16. Found: C, 79.00; H, 7.73; N, 5.91. UV λ_{max}^{MeOH} nm: 205, 258, 270, 285 (sh). IR ($CHCl_3$): 1640 cm^{-1}. NMR ($CDCl_3$) δ: 0.67 (3H, s), 1.30 (3H, s), 1.65—2.15 (2H, m), 2.73 (1H, q, J=6 Hz), 3.13 (1H, dt, J=8, 12 Hz), 3.20 (1H, d, J=6 Hz), 4.20 (1H, t, J=6 Hz), 4.47 (1H, dt, J=6, 12 Hz), 6.9—7.5 (3H, m), 7.95—8.2 (1H, m).

The ene-product (**10**). Yield: 7 mg (3%). Colorless oil. High-resolution MS m/z: M^+ Calcd for $C_{15}H_{17}NO$: 227.1309. Found: 227.1301. UV λ_{max}^{MeOH} nm: 204, 226, 253. IR ($CHCl_3$): 1640 cm^{-1}. NMR ($CDCl_3$) δ: 1.90 (3H, s), 1.9—2.4 (2H, m), 2.55—2.95 (2H, m), 3.05 (1H, q, J=6 Hz), 3.4—4.4 (3H, m), 4.75—5.1 (2H, m), 7.0—7.6 (3H, m), 7.9—8.2 (1H, m).

General Procedure for Photochemical Cycloreversion of the Parallel Adducts (2) to *o*-Vinylbenzamide Derivatives (3)——A solution of a parallel adduct (**2**, 0.3 mmol) in MeOH (40 ml) was irradiated at 300 nm for 45—120 min at room temperature. The solvent was evaporated off and the residue was chromatographed on silica gel with hexane–ether (3 : 1, v/v) to give the benzamide derivative (**3**).

1-(2-Vinylbenzoyl)-2-pyrroline (**3a**). Irradiation time: 45 min. Yield: 43 mg (72%). Colorless oil. High-resolution MS m/z: M^+ Calcd for $C_{13}H_{13}NO$: 199.0996. Found: 199.1019. UV λ_{max}^{MeOH} nm: 203, 242. IR ($CHCl_3$): 1630, 1615 cm^{-1}. NMR (CCl_4) δ: 2.40—2.85 (2H, m), 3.95 (2H, t, J=9 Hz), 4.97 (1H, dt, J=4, 2 Hz), 5.23 (1H, dd, J=10, 1.3 Hz), 5.63 (1H, dd, J=18, 1.3 Hz), 5.95 (1H, dt, J=4, 2 Hz), 6.70 (1H, dd, J=18, 10 Hz), 7.17—7.65 (4H, m).

1-(2-Vinylbenzoyl)-1,2,3,4-tetrahydropyridine (**3b**). Irradiation time: 60 min. Yield: 40 mg (63%). Colorless oil. High-resolution MS m/z: M^+ Calcd for $C_{14}H_{15}NO$: 213.1153. Found: 213.1186. UV λ_{max}^{MeOH} nm: 206, 241. IR ($CHCl_3$): 1620 cm^{-1}. NMR (CCl_4) δ: 1.6—2.3 (4H, m), 3.80 (2H, t, J=6 Hz), 4.70 (1H, dt, J=8, 4 Hz), 5.25 (1H, dd, J=10, 1.3 Hz), 5.65 (1H, dd, J=18, 1.3 Hz), 6.07 (1H, dt, J=8, 2 Hz), 6.70 (1H, dd, J=18, 10 Hz), 7.1—7.65 (4H, m).

1-[2-(2-Methyl-1-propenyl)benzoyl]-2-pyrroline (**3c**). Irradiation time: 120 min. The residue obtained after evaporation of the solvent was chromatographed on silica gel with hexane–ether (4 : 1, v/v) to give first the benzamide (**3c**), then the starting material (**2c**), and finally the ene-product (**10**) in yields of 21, 19, and 6%, respectively. The last two products (**2c** and **10**) were identified by mixture melting point determination as well as comparison of the spectral data with those of authentic samples. Longer irradiation did not cause any appreciable further consumption of the starting material.

The product (**3c**). Colorless oil. High-resolution MS m/z: M^+ Calcd for $C_{15}H_{17}NO$: 227.1309. Found: 227.1323. UV λ_{max}^{MeOH} nm: 205, 237. IR ($CHCl_3$): 1630, 1610 cm^{-1}. NMR (CCl_4) δ: 1.70 (3H, s), 1.85 (3H, s), 2.3—2.9 (2H, m), 3.92 (2H, t, J=9 Hz), 4.97 (1H, dt, J=4, 2 Hz), 5.93 (1H, dt, J=4, 2 Hz), 6.2 (1H, br s), 6.9—7.4 (4H, m).

1-(2-Ethylbenzoyl)pyrrolidine (4)——A solution of the *o*-vinylbenzamide (**3a**, 100 mg, 0.5 mmol) and 10% Pd–C (20 mg) in methanol (10 ml) was hydrogenated in an atmosphere of hydrogen for 1 h. The catalyst was filtered off and the filtrate was evaporated. The residue obtained after evaporation of the solvent was chromatographed on silica gel with hexane–ether (1 : 3, v/v) to give the product (**4**). Yield: 90 mg (89%). Colorless oil. High-resolution MS m/z: M^+ Calcd for $C_{13}H_{17}NO$: 203.1309. Found: 203.1303. UV λ_{max}^{MeOH} nm: 264 (sh), 270 (sh). IR ($CHCl_3$): 1615 cm^{-1}. NMR ($CDCl_3$) δ: 1.13 (3H, t, J=7.5 Hz), 1.67—2.05 (4H, m), 2.60 (2H, q, J=7.5 Hz), 3.07 (2H, t, J=7 Hz), 3.60 (2H, t, J=7 Hz), 7.10—7.30 (4H, m).

1-(2-Ethylbenzyl)pyrrolidine (5)——Compound **4** (62 mg, 0.31 mmol) in dry THF (2 ml) was added to a suspension of $LiAlH_4$ (70 mg) in dry THF (8 ml) and the whole was refluxed for 30 min. After addition of ether saturated with water followed by stirring for 1 h, the whole was dried on anhydrous Na_2SO_4. Evaporation of the solvent gave a colorless oil, 69 mg (67%). Picrate, mp 108—110 °C (EtOH).

5. High-resolution MS m/z: M^+ Calcd for $C_{13}H_{19}N$: 189.1517. Found: 189.1502. NMR (CCl_4) δ: 1.20 (3H, t, J=7.5 Hz), 1.6—1.9 (4H, m), 2.23—2.60 (4H, m), 2.73 (2H, q, J=7.5 Hz), 3.57 (2H, s), 6.95—7.30 (4H, m).

Picrate of **5**: *Anal.* Calcd for $C_{19}H_{22}N_4O_7$: C, 54.54; H, 5.30; N, 13.39. Found: C, 54.23; H, 5.19; N, 13.17.

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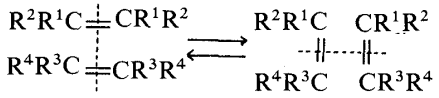
References and Notes

1) Part XXIII of "Cycloadditions in Syntheses." For Part XXII, see, N. Katagiri, M. Sato, T. Naito, M. Muto, T. Sakamoto, S. Saikawa, and C. Kaneko, *Tetrahedron Lett.*, **25**, 5665 (1984).
2) G. R. Evanega and D. L. Fabiny, *Tetrahedron Lett.*, **1971**, 1749.
3) T. Naito and C. Kaneko, *Tetrahedron Lett.*, **22**, 2671 (1981).
4) When olefins are treated with certain catalysts, they are converted to other olefins in a reaction in which the alkylidene groups (R^1R^2C=) become interchanged by a process schematically illustrated by the equation:



The reaction is called metathesis of olefins.

5) Recently, photochemical cycloaddition of cyclobutenes to cyclohexenones, followed by thermolysis of these photoadducts, has been widely used for the synthesis of 1,5-cyclodecadiene ring systems. The method is called photothermal olefin metathesis: *a*) P. A. Wender and J. C. Lechleiter, *J. Am. Chem. Soc.*, **99**, 267 (1977); *idem, ibid.*, **102**, 6341 (1980); *b*) G. L. Lange and F. C. McCarthy, *Tetrahedron Lett.*, **1978**, 4747; *c*) J. W. Williams and J. F. Callahan, *J. Chem. Soc., Chem. Commun.*, **1979**, 404.
6) 2-(5-Hexenyl)isoquinolin-1(2*H*)-one was also transformed to a single adduct (mp 72—74 °C, 65%) by irradiation at 350 nm. It is not yet known whether the adduct has a parallel or cross addition structure, but irradiation of the adduct at 300 nm was found to give a photo-equilibrated mixture of the adduct and the isoquinolone in a ratio of *ca.* 5 : 3. Structure determination of the adduct is in progress, and the result will be reported in due course.
7) Though the yield of **8** was only 1% when irradiation ($\geq$ 300 nm) was terminated as soon as almost all of **6** was consumed, the yield increased gradually when irradiation was continued further.
8) C. Kaneko and T. Naito, *Heterocycles*, **19**, 2183 (1982); T. Naito and C. Kaneko, *Yuki Gosei Kagaku Kyokai Shi*, **42**, 51 (1984).
9) The adduct (**7e**) was synthesized by irradiation of **6** at $\geq$ 300 nm in methanol–acetone (2 : 3, v/v) under bubbling of ethylene. Acetone was used to increase the solubility of ethylene in the irradiated solution.
10) If such radicals (B′ without the methylene bridge) are formed from intermolecular adducts (**7**), they presumably revert to the original cyclobutane compounds (**7**). This possibility is not excluded at present.
11) Recently, an exactly reverse type of reaction from *o*-vinylbenzamide derivatives to isoquinolin-1(2*H*)-ones was reported: A. Kasahara, T. Izumi, and O. Saito, *Chem. Ind.* (London), **1980**, 666.
12) Stork *et al.* recently utilized **11** and **12** to construct a functionalized galanthan ring: *a*) D. J. Morgan, Jr. and G. Stork, *Tetrahedron Lett.*, **1979**, 1959; *b*) G. Stork and D. J. Morgan, Jr., *J. Am. Chem. Soc.*, **101**, 7110 (1979).