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Novel Annelation Method to Pyridine and Isoquinoline by Photochemical Means[1]

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Intramolecular photoaddition reactions of 2-(ω-alkenyl)isoquinolin-1(2*H*)-ones and 1-(ω-alkenyl)pyridin-2(1*H*)-ones were examined, and the regioselectivity and dependence of these reactions on the length of methylene chain in the alkenyl group were clarified. By utilizing these reactions, a synthetic route to indolizine and quinolizine derivatives was elaborated. By an extension of this approach to the intermolecular reaction, 6-methoxy-3-methyl-1,2-dihydrocyclobuta[*b*]pyridin-4(3*H*)-one was synthesized from 4,6-dimethoxy-1-methylpyridin-2(1*H*)-one.

Keywords——2+2 photocycloaddition; intramolecular photoaddition; photocycloreversion; annelation; indolizine; quinolizine; cyclobuta[*b*]pyridine; 4,6-dimethoxypyridin-2(1*H*)-one; 1-(ω-alkenyl)pyridin-2(1*H*)-one; 2-(ω-alkenyl)isoquinolin-1(2*H*)-one

Previously, we reported that irradiation of 2-(ω-alkenyl)isoquinolin-1(2*H*)-ones (I, $n=2$, 3) in methanol at 350 nm afforded the parallel [2+2] adducts (II), which, though stable to irradiation at 350 nm, gave *o*-vinylbenzamide derivatives (III) on irradiation at 300 nm, and we designated the entire sequence as photo-photo olefin metathesis.[2] It was observed that the initial photoaddition step in the above metathesis proceeded much more efficiently than the corresponding intermolecular addition reaction between 1-isoquinolone and alkenes.[3,4] This fact as well as the regiospecific formation of the parallel adduct (II) shows clearly that the intramolecular addition reaction (I→II) is assisted by favorable entropy effects when the number of methylene units in I is two or three.[5]

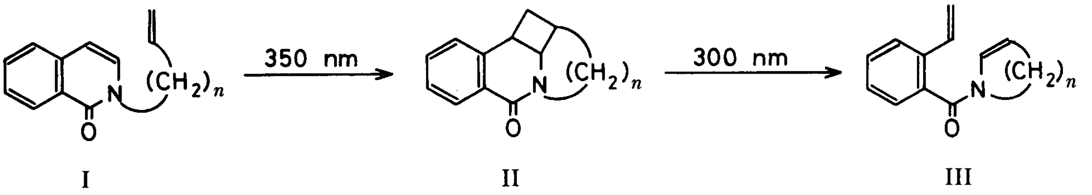
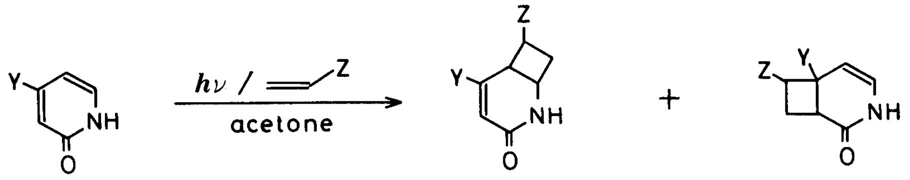


Chart 1

We[6] and others[7] have also shown that irradiation of 2-pyridones (IV) at ≥300 nm in acetone in the presence of olefins affords two kinds of [2+2] adducts (V and VI), whose proportions depend on the kind of olefins used as the counterpart of the photoaddition reactions. Thus, the adducts of type V are obtained predominantly when an electron-poor olefin is used, while adducts (VI) of the other type are formed almost exclusively when an electron-rich olefin is used.

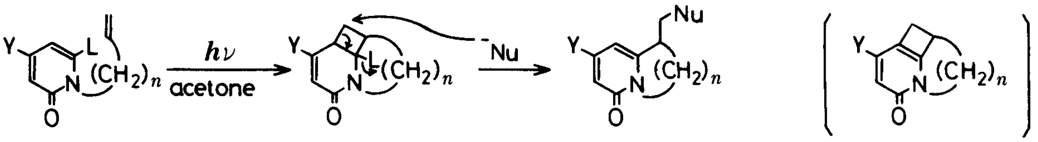
It is therefore expected that if the above-mentioned entropy effects also exist in the photoreaction of 1-(ω-alkenyl)pyridin-2(1*H*)-ones (VII), the corresponding parallel adducts (VIII) might be obtained, even if the terminal C=C bond is electron-rich. Furthermore, if the



IV V VI.

Chart 2

2-pyridone (VII) carries an appropriate leaving group at the 6-position, the adduct (VIII) may be either cleaved by the reaction with suitable nucleophiles to give annelated pyridones (IX) or transformed to the tricyclic compounds (X) having an aromatized pyridone ring (Chart 3).



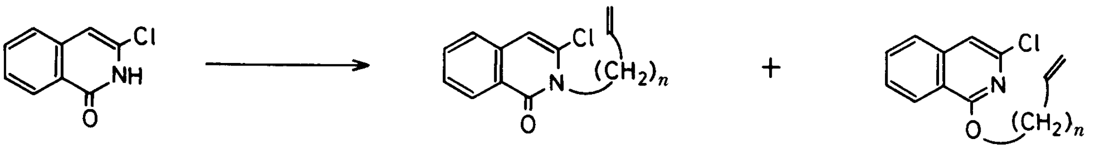
VII VIII IX X

Chart 3

In order to realize such transformations using appropriate isoquinolones and pyridones, we have undertaken systematic investigations and this paper reports the results in detail.

Photoreactions of 2-(ω-Alkenyl)-3-chloroisoquinolin-1(2*H*)-ones

Initially, we examined the photochemical behavior of 2-(ω-alkenyl)isoquinolin-1(2*H*)-ones (**2a**—**2c**) having a chlorine atom at the 3-position. These experiments would show not only whether the same transformations as observed in the 3-unsubstituted isoquinolones (Chart 1) are possible or not, but also the feasibility of the transformation of VIII to IX or X, giving annelated isoquinolones *via* the photoadducts having a chlorine atom as the leaving group. As detailed in Experimental, the starting materials (**2a**—**2c**) were synthesized from 3-chloroisoquinolin-1(2*H*)-one (**1**)[8] by treatment with ω-alkenyl bromide under basic conditions using a phase transfer catalyst. In all cases, the *O*-alkenylated products (**3a**—**3c**) were obtained as byproducts (Chart 4).



1 **2** **3**

	n
a	2
b	3
c	4

Chart 4

Irradiation of 3-chloro-2-(3-butenyl)isoquinolin-1(2*H*)-one (**2a**) in methanol at 350 nm until almost all of the starting material had been consumed afforded a tetracyclic and two tricyclic products (**4a**, **5**, and **6**) in yields of 32, 30, and 4%, respectively. Though the nuclear magnetic resonance (NMR) spectrum of **5** was somewhat complex, its monodeuterated product (**5**-1-d) obtained by treatment with deuteriomethanol under basic conditions showed a singlet at 3.62 due to the methoxymethyl group. The same types of products were also obtained when irradiation was performed in ethanol. When 3-chloro-2-(4-pentenyl)isoquinolin-1(2*H*)-one (**2b**) was irradiated under the same conditions, only the tetracyclic product (**4b**) was obtained in 57% yield. On the other hand, only the tricyclic compound (**7**) was obtained when 3-chloro-2-(5-hexenyl)isoquinolin-1(2*H*)-one (**2c**) was irradiated under the same irradiation conditions.

These experiments show clearly that all reactions proceed *via* the corresponding [2+2] adducts and these are parallel adducts (**8**) when the alkenyl group in **2** has two or three methylenes, whereas the isoquinolone having a four methylene chain (**2c**) affords the cross adduct (**9**) as the primary product. The regioselectivity of the intramolecular photoaddition reactions of **2** is therefore the same as that found in the corresponding 3-unsubstituted isoquinolones.[2]

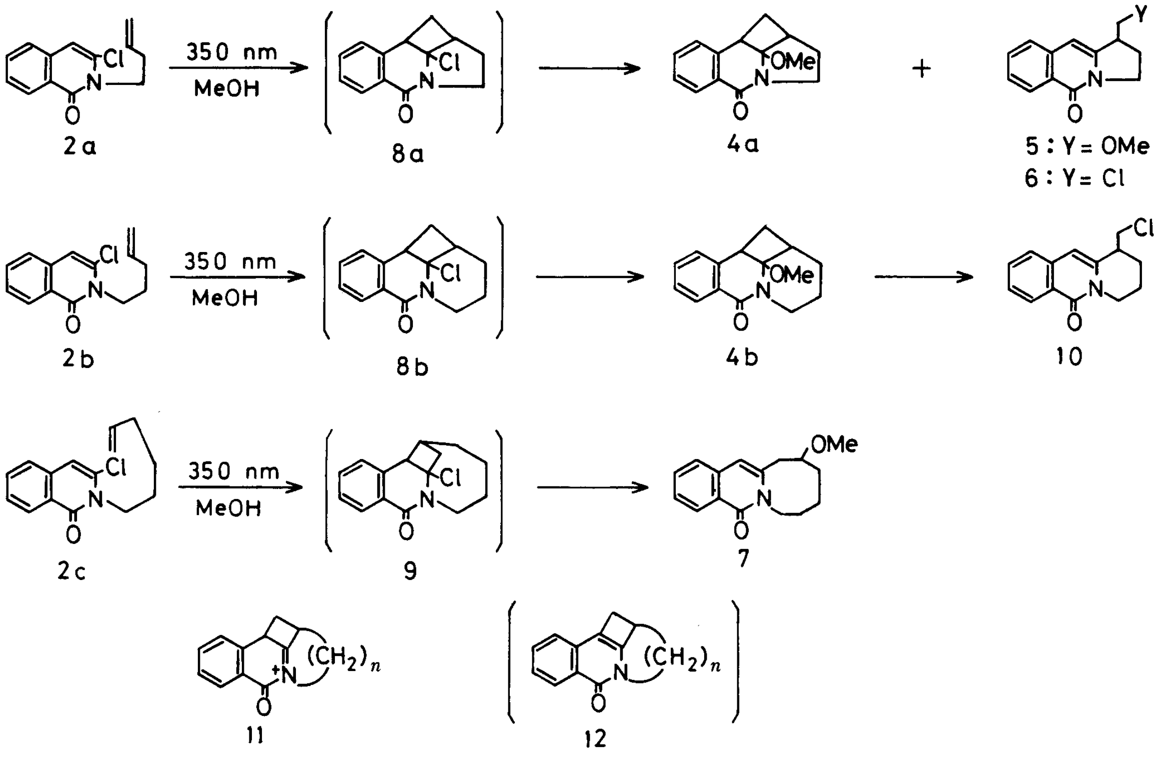


Chart 5

Since they have a reactive α-chloroalkylamine structure, these adducts (**8a** and **8b**) not only afford the tetracyclic products (**4a** and **4b**) by direct replacement of the chlorine atom with a methoxyl group, but also give the tricyclic products (**5** and **6**) by fission of the C–C bond involved in the strained cyclobutane ring of the iminium cation species (**11**) with concomitant attack of nucleophiles (MeOH or Cl^-). In accordance with this mechanism, when **2a** was irradiated in acetonitrile under the same conditions, the tricyclic product (**6**) was obtained as the sole product. Furthermore, when the tetracyclic compounds (**4a** and **4b**) were refluxed in methanol containing concentrated hydrochloric acid, the corresponding tricyclic compounds (**5**, **6**, and **10**) were obtained. A similar iminium cation derived from the cross adduct (**9**) may also account for the direct formation of **7** from **2c**. The fact that **12** was not obtained in any case shows that the ring system (X) is highly strained due to the presence of the methylene bridge, though 1,2-dihydrocyclobuta[*c*]isoquinolin-4(3*H*)-ones without the methylene bridge were synthesized previously.[4a,b]

The fact that the cycloreversion reactions (*cf.* II→III)[2] still occur in these tetracyclic compounds (**4**) is demonstrated by the formation of *o*-vinylbenzamide derivatives (**14**) when the former compounds are irradiated in methanol at 300 nm. The enol ether function in the direct cycloreversion products (**13**) is too unstable for these products to be isolable, and they are transformed to **14** during the reaction (Chart 6).

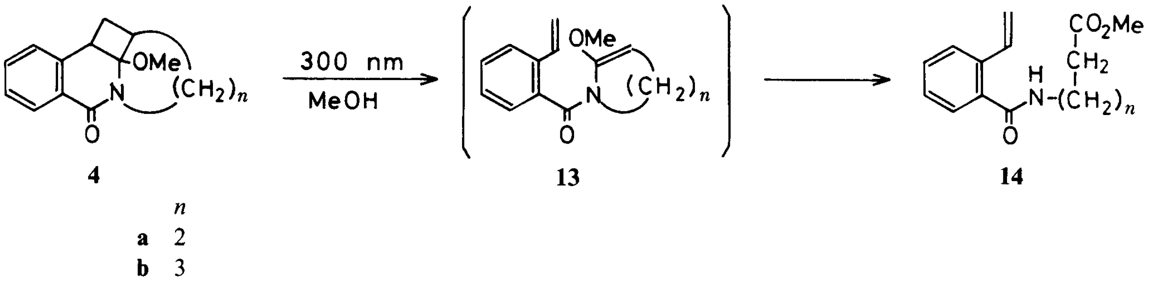


Chart 6

Hence, we have established a new method for annelation of three- to four-methylene chains at the 2,3-position of 1-isoquinolone ring, giving benzo-fused indolizine and quinolizine rings having a C-1 unit at the 1-position.

Photoreactions of 1-(ω-Alkenyl)pyridin-2(1*H*)-ones

The method developed for the annelation of 1-isoquinolones as described above was then applied to the 2-pyridone series in order to establish a new entry to the indolizine or quinolizine ring system.

Generally, photoreactions of 2-pyridones are more complex than those of their benzo-analogues. In monocyclic heteroaromatics such as 2-pyridones and uracils, intersystem crossing from S_1 to T_1 is far less efficient than in the bicyclic series.[9] Hence, in order to generate the T_1 state, which is responsible for the cycloaddition reactions, the irradiation must be carried out in the presence of suitable sensitizers (*e.g.* acetone). However,this sensitized irradiation technique results in self-polymerization of the olefins used in conjuction with the desired reaction. Furthermore, dimerization of 2-pyridones under either direct or sensitized conditions is a more efficient process than that of their benzenoid homologues.[10] In connection with the above problems, we previously investigated the intermolecular photo-addition of 2-pyridones to olefins and found that 2-pyridones having a 4-alkoxyl group are the most suitable materials for this reaction because of their inability to photodimerize.[6]

Accordingly, a general method for the synthesis of 6-substituted pyridin-2(1*H*)-ones with or without a 4-alkoxy group was first explored. We chose 2,6-dichloropyridine (**15**) as the common starting material, as detailed in Experimental, and have elaborated a method to covert **15** to a series of 6- and 4,6-disubstituted pyridin-2(1*H*)-ones in which the 6-substituent is either methoxyl or chlorine (both are able to act as the leaving group) and the 4-substituent is a methoxyl group (Chart 7).

Two pyridones (**16** and **17**) were synthesized previously from **15**.[11,12] The general strategy we employed is the same as that involved in the synthesis of **17** from **15**.[12] Thus, successive replacement of the chlorine atoms of **15** with methoxyl groups gave first 2-chloro-6-methoxypyridine and finally 2,6-dimethoxypyridine, which, on removal of a methyl group under acidic conditions, afforded **17**. We have found that the use of a benzyloxy group in the second step is an attractive alternative for the synthesis of **17**, because debenzylation can be accomplished readily by catalytic hydrogenation. In the same manner, syntheses of **18** and **19** were accomplished *via* 2,4,6-trichloropyridine (**21**) as a common intermediate. The synthesis of **21** was achieved by *N*-oxidation of **15** to give **20**[13] followed by treatment with phosphorus oxychloride.

These 6-substituted pyridines (**16** and **17**) as well as their 4-methoxy derivatives (**18** and **19**) gave the 1-(ω-alkenyl)pyridin-2(1*H*)-ones (**22**—**25**) on treatment with ω-alkenyl bromide

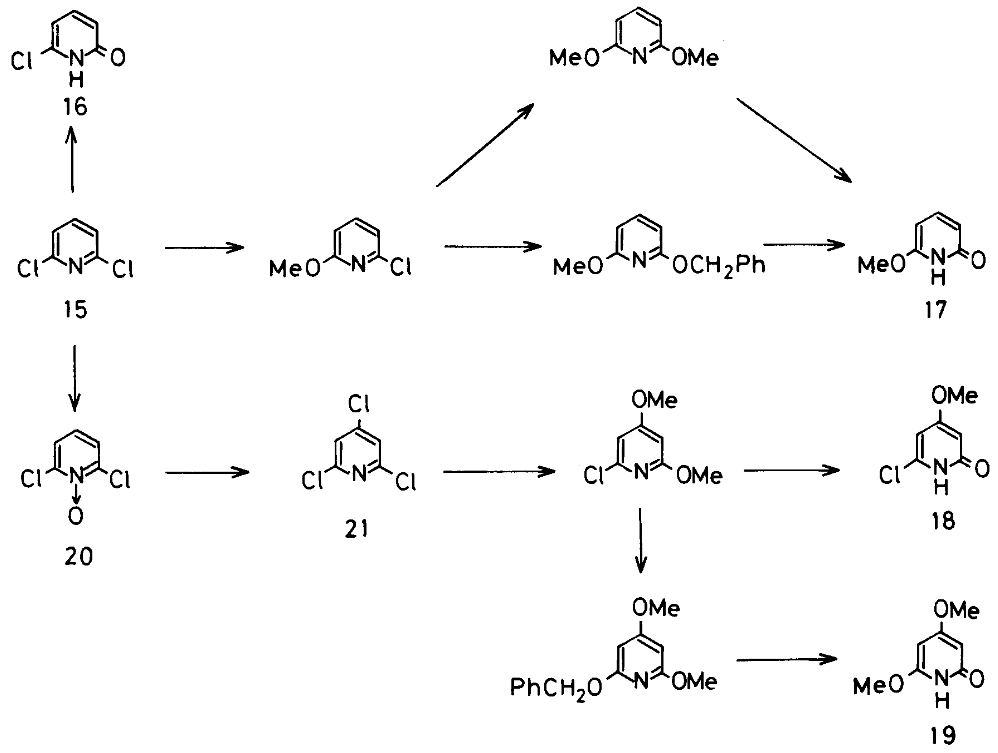


Chart 7

under basic conditions, just as in the synthesis of the corresponding isoquinolones (**2a**—**2c**). It should be noted that though alkenylation of 2-pyridone itself as well as its 4-methoxy derivative afforded the *N*-substituted derivatives (**26** and **27**) almost exclusively, these 6-substituted pyridin-2(1*H*)-ones (**16**—**19**) gave the *O*-substituted products (**28**—**31**) in higher yields than the *N*-substituted ones (**22**—**25**).

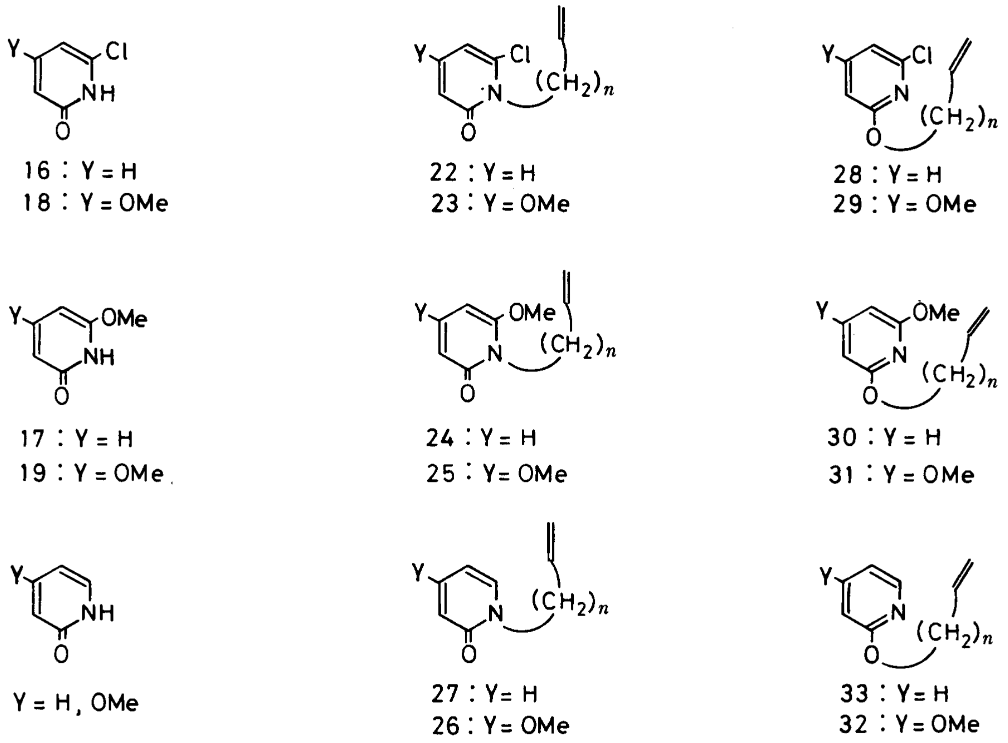


Chart 8 ($n=2$—4)

Irradiation of 6-chloropyridin-2(1*H*)-one derivatives (**22** and **23**) in acetone afforded the bicyclic products (**34** and **35**), presumably through the corresponding parallel adducts (**40** and **41**). As expected, the parallel adducts (**36** and **37**) were obtained directly by irradiation of 6-methoxypyridin-2(1*H*)-ones (**24** and **25**) under the same conditions. It is noteworthy that the yields (*ca.* 70%) of **37** from 4-methoxypyridin-2(1*H*)-ones are higher than those (*ca.* 45%) of **36** from 4-unsubstituted ones. Though irradiation of **26** also afforded the parallel adduct (**38**), its nor-methoxy derivative (**27**) did not give the corresponding adduct (**39**). These results indicate that the presence of a 4-methoxyl group in the 2-pyridone ring enhances the reactivity of the C_5–C_6 double bond toward photocycloaddition reactions. The same accelerating effects are also evident with a 6-methoxy group in the pyridone ring, because the 6-methoxy derivatives (**24** and **25**) always gave the adducts (**36** and **37**) in higher yields than those of the corresponding 6-unsubstituted compounds (**26** and **27**), and no adduct at all was obtained by irradiation of **27** ($n=3$). It should be noted that none of the 2-pyridones so far examined gave the cyclized product when they carried an alkenyl group having a four-methylene chain. This fact indicates that the intramolecular addition reactions of 1-(ω-alkenyl)pyridin-2(1*H*)-ones are less efficient than those of the corresponding isoquinolones, because in the latter case the product (**7**) formed *via* the cross adduct (**9**) was obtained from **2c**.

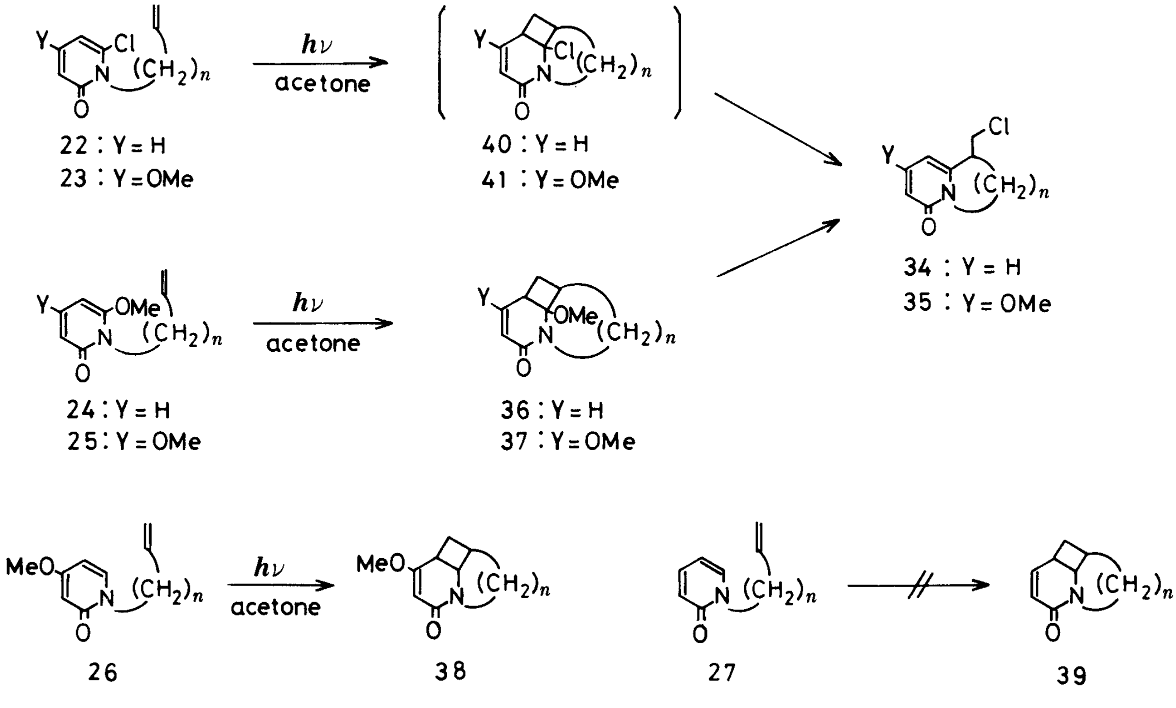


Chart 9 ($n=2, 3$)

Finally, we wish to comment on the successful transformation of the adducts (**36** and **37**) to bicyclic compounds (**34** and **35**). These reactions were best carried out by treatment of the former compounds with stannic chloride in benzene.

Thus, we have established a new route to either 5-oxo-1,2,3,5-tetrahydroindolizines (**34** and **35**; $n=2$) or 6-oxo-1,3,4,6-tetrahydroquinolizines (**34** and **35**; $n=3$) having a chloromethyl group at the 1-position. Both of these nuclei are familiar in the alkaloid field, and **34** and **35** ($n=3$) have a carbon skeleton identical with that of lupinine, an alkaloid contained in *Lupinus* species.

Synthesis of 6-Methoxy-3-methyl-1,2-dihydrocyclobuta[*b*]pyridin-4(3*H*)-one

Previously, we established a two-step synthetic method for 1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one and its 1-substituted derivatives from 4-methoxypyridin-2(1*H*)-one, by the addition of the latter (*via* T_1) to olefins followed by elimination of methanol from the adducts (Chart 10).[6)]

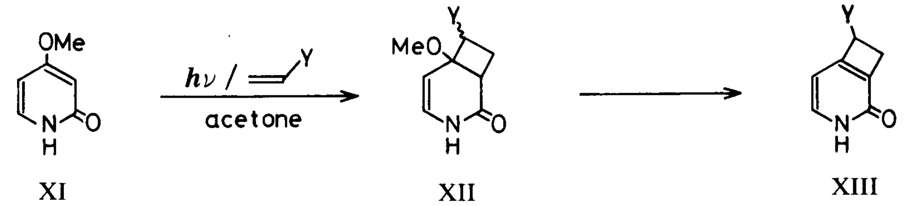


Chart 10

Since we found that 4,6-dimethoxy-1-(ω-alkenyl)pyridin-2(1*H*)-ones (**25**; $n=2$, 3) cyclized *via* the T_1 state most efficiently among the 2-pyridones examined, we next examined the intermolecular photoaddition of 4,6-dimethoxy-1-methylpyridin-2(1*H*)-one[14)] to olefins. Irradiation of 4,6-dimethoxy-1-methylpyridin-2(1*H*)-one (**42**) in acetone under bubbling of ethylene afforded a single photoadduct in 9% yield. The basic structure of the adduct was deduced to be 2-azabicyclo[4.2.0]oct-4-en-3-one (**43**) and not 3-azabicyclo[4.2.0]oct-4-en-2-one (**45**) from the results of both ultraviolet (UV) and NMR spectroscopy. Thus, the UV spectrum of the adduct was almost superimposable on those of **37** ($n=2$, 3) and differed markedly from those of the intermolecular adducts (VI; Chart 2) obtained in our previous study.[6)] The NMR spectrum of the adduct (**43**) showed the signal of the olefinic proton (C_4-H) at 5.08 as a sharp singlet, indicating that there is no long-range coupling between C_4-H and C_6-H. We noted previously that while the adducts of type V show no such coupling, the adducts of type VI exhibit an appreciable coupling (*ca.* 2 Hz) between the olefinic pooton (C_5-H) and C_1-H. These observations clearly indicate that the adduct has the structure **43** and not **45**. Refluxing of **43** in benzene containing potassium *tert*-butoxide then afforded the corresponding cyclobuta[*b*]pyridone (**44**) in 75% yield as the sole product.

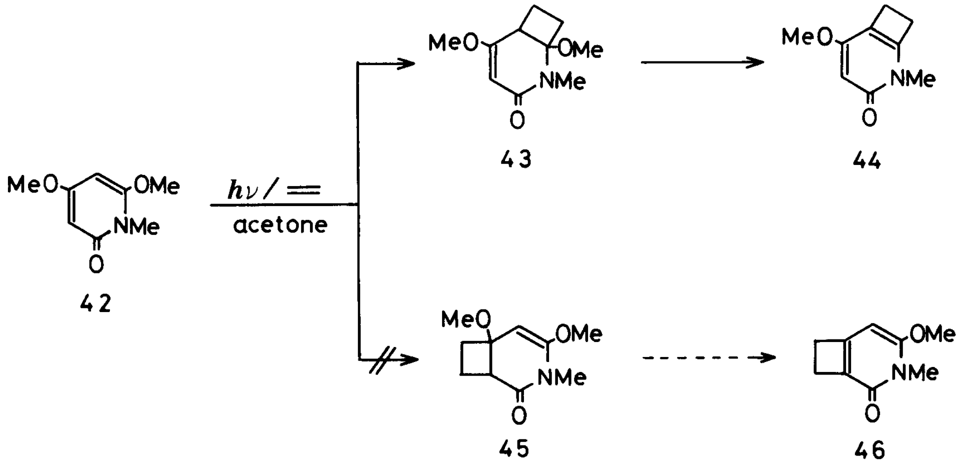


Chart 11

Two important points arise from the above results. First, the pyridone (**42**) can add to ethylene itself and the addition of the pyridone ring to ethylene occurs regiospecifically across its C_5–C_6 double bond. Secondly, considering the previous results (*vide supra*), an efficient synthetic route to 1,2-dihydrocyclobuta[*b*]pyridin-4(3*H*)-ones from **42** is expected to be possible by using an electron-poor olefin as the counterpart of the photoaddition reaction.[15)]

Conclusions

We have developed a photochemical method for the annelation of 1-isoquinolone at its [*b*]-bond position using 2-(ω-alkenyl)isoquinolin-1(2*H*)-ones having a suitable leaving group at the 3-position. An extension of the method to the pyridone series has led to a general synthetic method for indolizine and quinolizine derivatives having a C_1-unit at the 1-position. The regioselectivity and dependence of the reaction on the length of the methylene chain were established in the intramolecular photoaddition reactions of these *N*-(ω-alkenyl)pyridones and isoquinolones. Finally, based on the substituent effects clarified in the above study, we have synthesized 6-methoxy-3-methyl-1,2-dihydrocyclobuta[*b*]pyridin-4(3*H*)-one from 4,6-dimethoxy-1-methylpyridin-2(1*H*)-one and ethylene by photochemical means. We propose that the use of an electron-poor olefin instead of ethylene may provide a new preparative route to cyclobuta[*b*]pyridone derivatives.

Experimental

All melting points were determined on a Yanagimoto micromelting point apparatus (hot stage type) and are uncorrected. Infrared (IR) spectra were taken on a JASCO A-102 spectrometer. ^{1}H-NMR spectra were taken on a JEOL PMX 60 or a JEOL FX-100 spectrometer using tetramethylsilane as an internal standard. Mass spectra (MS) were measured with a Hitachi M-52G or a JEOL JNM-01SG-2 spectrometer. UV spectra were recorded on a Hitachi 320 spectrometer. Column chromatography was performed on silica gel (Wakogel C-200) and preparative thin-layer chromatography (PTLC) on Silica gel GF_{254} (type 60, Merck).

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

b) Irradiation at 300 or 350 nm: Irradiation at the specified wavelength was performed in a quartz vessel using Rayonet photochemical reactor lamps (RPR-3000 Å or RPR-3500 Å). Argon was bubbled through the solution for 10 min before the irradiation was started.

Synthesis of 2-(ω-Alkenyl)-3-chloroisoquinolin-1(2*H*)-ones (2a—c)——Synthesis of 2-(3-Butenyl)-3-chloroisoquinolin-1(2*H*)-one (**2a**) 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 **1**[8] (1.8 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, then with 5% HCl, and finally with water, and dried (Na_2SO_4). The residue obtained after evaporation of the solvent was chromatographed on silica gel. Elution with CH_2Cl_2–hexane (5 : 1, v/v) gave 0.91 g (39%) of **3a**. Elution with CH_2Cl_2 gave 1.13 g (48%) of **2a**.

2a. Colorless oil. High-resolution MS *m*/*z*: M^+ Calcd for $C_{13}H_{12}ClNO$: 233.0607 (^{35}Cl) and 235.0578 (^{37}Cl). Found: 233.0619 and 235.0583. IR ($CHCl_3$): 1655, 1615 cm^{-1}. ^{1}H-NMR (CCl_4): 2.3—2.8 (2H, m), 4.1—4.4 (2H, m), 4.7—5.2 (2H, m), 5.4—6.2 (1H, m), 6.47 (1H, s), 7.1—7.6 (3H, m), 8.1—8.4 (1H, m).

1-(3-Butenyloxy)-3-chloroisoquinoline (**3a**). Colorless oil. High-resolution MS *m*/*z*: M^+ Calcd for $C_{13}H_{12}ClNO$: 233.0607 (^{35}Cl) and 235.0578 (^{37}Cl). Found: 233.0603 and 235.0578. IR ($CHCl_3$): 1620 cm^{-1}. ^{1}H-NMR (CCl_4) δ: 2.3—2.85 (2H, m), 4.50 (2H, t, J=6.5 Hz), 4.9—5.25 (2H, m), 5.55—6.25 (1H, m), 7.10 (1H, s), 7.1—7.6 (3H, m), 7.9—8.2 (1H, m).

The following compounds were prepared in the same manner.

3-Chloro-2-(4-pentenyl)isoquinolin-1(2*H*)-one (**2b**). Yield: 40%. Colorless oil. High-resolution MS *m*/*z*: M^+ Calcd for $C_{14}H_{14}ClNO$: 247.0763 (^{35}Cl) and 249.0735 (^{37}Cl). Found: 247.0784 and 249.0755. IR ($CHCl_3$): 1650, 1615 cm^{-1}. ^{1}H-NMR (CCl_4) δ: 1.5—2.5 (4H, m), 4.1—4.4 (2H, m), 4.9—5.3 (2H, m), 5.5—6.2 (1H, m), 6.45 (1H, s), 7.15—7.75 (3H, m), 8.2—8.45 (1H, m).

3-Chloro-1-(4-pentenyloxy)isoquinoline (**3b**). Yield: 35%. Colorless oil. High-resolution MS *m*/*z*: M^+ Calcd for $C_{14}H_{14}ClNO$: 247.0763 (^{35}Cl) and 249.0735 (^{37}Cl). Found: 247.0784 and 249.0753. IR ($CHCl_3$): 1620 cm^{-1}. ^{1}H-NMR (CCl_4) δ: 1.6—2.5 (4H, m), 4.50 (2H, t, J=6.5 Hz), 4.8—5.25 (2H, m), 5.5—6.25 (1H, m), 7.10 (1H, s), 7.2—7.7 (3H, m), 7.95—8.3 (1H, m).

3-Chloro-3-(5-hexenyl)isoquinolin-1(2*H*)-one (**2c**). Yield: 50%. Colorless oil. High-resolution MS *m*/*z*: M^+ Calcd for $C_{15}H_{16}ClNO$: 261.0920 (^{35}Cl) and 263.0891 (^{37}Cl). Found: 261.0945 and 263.0918. IR ($CHCl_3$): 1655, 1615 cm^{-1}. ^{1}H-NMR (CCl_4) δ: 1.15—2.4 (6H, m), 4.0—4.2 (2H, m), 4.7—5.2 (2H, m), 5.4—6.2 (1H, m), 6.43 (1H, s), 7.15—7.7 (3H, m), 8.1—8.4 (1H, m).

3-Chloro-1-(5-hexenyloxy)isoquinoline (**3c**). Yield: 32%. Colorless oil. High-resolution MS *m*/*z*: M^+ Calcd for $C_{15}H_{16}ClNO$: 261.0920 (^{35}Cl) and 263.0891 (^{37}Cl). Found: 261.0948 and 263.0920. IR ($CHCl_3$): 1620 cm^{-1}. ^{1}H-NMR

(CCl_4) δ: 1.2—2.4 (6H, m), 4.47 (2H, t, J=6 Hz), 4.8—5.2 (2H, m), 5.5—6.2 (1H, m), 7.10 (1H, s), 7.2—7.6 (3H, m), 7.9—8.3 (1H, m).

Irradiation of 2a——(A) In Methanol: A solution of **2a** (234 mg, 1 mmol) in methanol (120 ml) was irradiated at 350 nm for 30 min. The solvent was evaporated off and the residue was chromatographed on silica gel. Elution with hexane–ether (2 : 1, v/v) gave 74 mg (32%) of the parallel adduct (**4a**). Elution with hexane–ether (1 : 1, v/v) gave 10 mg (4%) of **6**. Elution with ether gave 69 mg (30%) of **5**.

9c-Methoxy-5-oxo-1a,2,3,5,9b,9c-hexahydro-1*H*-cyclobuta[*hi*]benzo[*f*]indolizine (**4a**). Colorless prisms, mp 85—86 °C (hexane). High-resolution MS *m*/*z*: M$^+$ Calcd for $C_{14}H_{15}NO_2$: 229.1102. Found: 229.1105. IR (KBr): 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.0—1.4 (1H, m), 1.5—1.95 (1H, m), 2.0—2.4 (1H, m), 2.4—3.0 (2H, m), 3.05 (3H, s), 3.2—3.8 (2H, m), 4.52 (1H, ddd, J=3, 9, 12 Hz), 7.0—7.5 (3H, m), 7.9—8.15 (1H, m).

1-Methoxymethyl-5-oxo-1,2,3,5-tetrahydropyrrolo[1,2-*b*]isoquinoline (**5**). Colorless prisms, mp 120—121 °C (ether–hexane). High-resolution MS *m*/*z*: M$^+$ Calcd for $C_{14}H_{15}NO_2$: 229.1102. Found: 229.1104. IR (KBr): 1668, 1642, 1621 cm^{-1}. MS *m*/*z*: 229 (M$^+$), 184 (M$^+$ $-CH_2OMe$). ^{1}H-NMR ($CDCl_3$) δ: 1.75—2.55 (2H, m), 3.3—3.9 (3H, m), 3.40 (3H, s), 3.95—4.45 (2H, m), 6.50 (1H, s), 7.1—7.8 (3H, m), 8.3—8.5 (1H, m).

1-Chloromethyl-5-oxo-1,2,3,5-tetrahydropyrrolo[1,2-*b*]isoquinoline (**6**). Colorless prisms, mp 115—117 °C (hexane–ether). High-resolution MS *m*/*z*: M$^+$ Calcd for $C_{13}H_{12}ClNO$: 233.0607 (^{35}Cl) and 235.0578 (^{37}Cl). Found: 233.0610 and 235.0588. IR (KBr): 1656, 1630, 1601 cm^{-1}. MS *m*/*z*: 235 and 233 (M$^+$), 184 (M$^+$ $-CH_2Cl$). ^{1}H-NMR ($CDCl_3$) δ: 1.9—2.7 (2H, m), 3.5—4.0 (3H, m), 4.0—4.45 (2H, m), 6.45 (1H, s), 7.3—7.8 (3H, m), 8.25—8.45 (1H, m).

(B) In Acetonitrile: Under the same irradiation conditions, except for the use of acetonitrile instead of methanol as the solvent, **6** was obtained in 30% yield as the sole product.

Conversion of 4a to 5——A solution of **4a** (14.8 mg, 0.065 mmol) in methanol (5 ml) containing conc. HCl (0.1 ml) was refluxed for 1.5 h. After evaporation of the solvent, the residue was purified by PTLC (5% MeOH–CH_2Cl_2) to give 10.3 mg (70%) of **5**. Though the formation of **6** was detected by TLC, it could not be isolated because of the small amount formed.

Deuteration of 5——Sodium metal (50 mg) was added to CD_3OD (2 ml). After addition of **5** (11.6 mg, 0.05 mmol) to this solution, the whole was refluxed for 2 h. The residue obtained after evaporation of the solvent was subjected to PTLC (5% MeOH–CH_2Cl_2) to give 6.8 mg (55%) of **5**-1-d as colorless prisms, mp 120—121 °C (MeOH). MS *m*/*z*: 230 (M$^+$), 185 (M$^+$ $-CH_2OMe$). IR (KBr): 1668, 1642, 1621 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.7—2.5 (2H, m), 3.62 (2H, br s), 3.40 (3H, s), 4.0—4.4 (2H, m), 6.48 (1H, s), 7.25—7.7 (3H, m), 8.1—8.35 (1H, m).

Irradiation of 2b in Methanol——A solution of **2b** (248 mg, 1 mmol) in methanol (120 ml) was irradiated at 350 nm for 30 min. The solvent was evaporated off and the residue was chromatographed on silica gel with hexane–ether (2 : 1, v/v) to give **4b** as the sole product.

10c-Methoxy-6-oxo-1a,3,4,6,10b,10c-hexahydro-1*H*,2*H*-cyclobuta[*ij*]benzo[*b*]quinolizine (**4b**). Yield: 139 mg (57%). Colorless needles, mp 142—143 °C (ether–hexane). *Anal.* Calcd for $C_{15}H_{17}NO_2$: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.92; H, 7.01; N, 5.58. IR (KBr): 1633 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.35—1.95 (5H, m), 2.0—2.4 (1H, m), 2.5—3.0 (3H, m), 2.98 (3H, s), 3.35 (1H, t, J=9 Hz), 4.4—4.7 (1H, m), 7.0—7.5 (3H, m), 8.0—8.2 (1H, m).

1-Chloromethyl-6-oxo-1,3,4,6-tetrahydro-2*H*-pyrido[1,2-*b*]isoquinoline (10)——A solution of **4b** (26 mg, 0.11 mmol) in methanol (7 ml) containing conc. HCl (0.1 ml) was refluxed for 4 h. The solvent was evaporated off and the residue was taken up in CH_2Cl_2. The organic layer was washed with aq. K_2CO_3 and dried (Na_2SO_4). The residue obtained after evaporation of the solvent was separated by PTLC (ether–hexane 5 : 1, v/v) to give **10**. Yield: 14.8 mg (57%). Colorless prisms, mp 96—99 °C (ethyl acetate). High-resolution MS *m*/*z*: M$^+$ Calcd for $C_{14}H_{14}ClNO$: 247.0762 (^{35}Cl) and 249.0734 (^{37}Cl). Found: 247.0760 and 249.0734. IR (KBr): 1638, 1620 cm^{-1}. MS *m*/*z*: 249 and 247 (M$^+$), 198 (M$^+$ $-CH_2Cl$). ^{1}H-NMR ($CDCl_3$) δ: 1.5—2.25 (4H, m), 2.9—3.3 (1H, m), 3.45—4.5 (4H, m), 6.34 (1H, s), 7.1—7.7 (3H, m), 8.05—8.35 (1H, m).

2-Methoxy-8-oxo-1,3,4,5,6,8-hexahydro-2*H*-azocino[1,2-*b*]isoquinoline (7)——A solution of **2c** (262 mg, 1 mmol) in methanol (120 ml) was irradiated at 350 nm for 4 h. The solvent was evaporated off and the residue was chromatographed on silica gel. Elution with hexane–ether (1 : 1, v/v) afforded **7**. Yield: 96 mg (37%). Colorless prisms, mp 141—143 °C (CH_2Cl_2–hexane). High-resolution MS *m*/*z*: M$^+$ Calcd for $C_{16}H_{19}NO_2$: 257.1415. Found: 257.1393. IR ($CHCl_3$): 1640, 1620 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.4—2.1 (6H, m), 2.89 (1H, dd, J=8, 14 Hz), 3.09 (1H, dd, J=4, 14 Hz), 3.2—3.5 (1H, m), 3.40 (3H, s), 3.8—4.2 (1H, m), 4.25—4.7 (1H, m), 6.36 (1H, s), 7.2—7.6 (3H, m), 8.15—8.3 (1H, m).

***N*-(ω-Methoxycarbonylalkyl)-2-vinylbenzamides (14)**——*N*-(3-Methoxycarbonylpropyl)-2-vinylbenzamide (**14a**) as a Typical Example: A solution of **4a** (69 mg, 0.3 mmol) in methanol (40 ml) was irradiated at 300 nm for 1 h. The solvent was evaporated off and the residue was chromatographed on silica gel. Elution with ether–hexane (1 : 1, v/v) gave **14a**. Yield: 26 mg (38%). Colorless oil. High-resolution MS *m*/*z*: M$^+$ Calcd for $C_{14}H_{17}NO_3$: 247.1207. Found: 247.1210. IR ($CHCl_3$): 1725, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.1 (2H, m), 2.30 (2H, t, J=6 Hz), 3.30 (2H, q, J=6 Hz), 3.60 (3H, s), 5.33 (1H, dd, J=10, 1.5 Hz), 5.57 (1H, dd, J=18, 1.5 Hz), 6.2—6.6 (1H, m), 7.00 (1H, dd, J=18, 10 Hz), 7.15—7.6 (4H, m).

The following compound (**14b**) was prepared from **4b** in the same manner.

N-(4-Methoxycarbonylbutyl)-2-vinylbenzamide (**14b**). Yield: 36%. Colorless oil. High-resolution MS *m*/*z*: M$^+$

Calcd for $C_{15}H_{19}NO_3$: 261.1364. Found: 261.1374. IR ($CHCl_3$): 1725, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.2—2.0 (4H, m), 2.0—2.5 (2H, m), 3.0—3.5 (2H, m), 3.60 (3H, s), 5.25 (1H, dd, $J=10$, 1.5 Hz), 5.60 (1H, dd, $J=17$, 1.5 Hz), 6.3—6.7 (1H, m), 7.03 (1H, dd, $J=17$, 10 Hz), 7.15—7.7 (4H, m).

2,6-Dichloropyridine-1-oxide (20)——A solution of 2,6-dichloropyridine (**15**: 12 g, 0.08 mol) in a mixture of CF_3CO_2H (100 ml) and 30% aq. H_2O_2 (14 ml) was heated on a boiling water bath for 3 h. After addition of 300 ml of water, the reaction mixture was concentrated *in vacuo* to *ca.* 50 ml and basified by the addition of $NaHCO_3$. The product was taken up in CH_2Cl_2, and the organic layer was separated and dried over K_2CO_3. The solvent was evaporated off and the residue was recrystallized from ethyl acetate to give **20**. Yield: 8.3 g (63%). Colorless prisms, mp 137—139 °C (lit.[13] mp 137 °C).

2,4,6-Trichloropyridine (21)——A mixture of **20** (4.92 g) and $POCl_3$ (10 ml) was refluxed for 4 h. After evaporation of the solvent *in vacuo*, the residue was poured onto crushed ice and basified by the addition of Na_2CO_3 and the product was taken up in ether. The organic layer was dried over K_2CO_3. The residue obtained after evaporation of the solvent was chromatographed on silica gel. Elution with hexane–ether (5 : 1, v/v) gave 4.04 g (73%) of **21**. Colorless needles (pentane), mp 33—34 °C (lit.[13] mp 32.5—33 °C).

2,4,6-Trimethoxypyridine——A solution of **21** (3.65 g, 20 mmol) in NaOMe/MeOH [prepared from 13.8 g (0.6 mol) of Na and 120 ml of methanol] was refluxed for 3.5 h on an oil bath (140 °C). The solvent was evaporated off and the residue after addition of water was taken up in CH_2Cl_2. The organic layer was washed with water and dried over $MgSO_4$. The residue obtained after evaporation of the solvent was recrystallized from pentane to give the trimethoxypyridine. Yield: 2.7 g (81%), colorless prisms, mp 47—48 °C (pentane). *Anal.* Calcd for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.28. Found: C, 56.67; H, 6.81; N, 8.11. ^{1}H-NMR ($CDCl_3$) δ: 3.75 (3H, s), 3.85 (6H, s), 5.83 (2H, s).

2-Chloro-4,6-dimethoxypyridine——A solution of **21** (1.83 g, 10 mmol) in NaOMe/MeOH (prepared from 1.15 g of Na and 20 ml of methanol) was refluxed for 7 h. The solvent was evaporated off and the residue after addition of water was taken up in CH_2Cl_2. The organic layer was washed with water and dried over $MgSO_4$. The solvent was evaporated off and the residue was chromatographed on silica gel. Elution with CH_2Cl_2–hexane (1 : 3, v/v) afforded first 393 mg (23%) of 4-chloro-2,6-dimethoxypyridine, then 943 mg (54%) of 2-chloro-4,6-dimethoxypyridine, and finally 320 mg (19%) of 2,4,6-trimethoxypyridine.

4-Chloro-2,6-dimethoxypyridine. Colorless prisms, mp 64—65 °C (MeOH). *Anal.* Calcd for $C_7H_8ClNO_2$: C, 48.43; H, 4.65; Cl, 20.42, N, 8.07. Found: C, 48.36; H, 4.63; Cl, 20.62; N, 8.04. ^{1}H-NMR ($CDCl_3$) δ: 3.90 (6H, s), 6.30 (2H, s).

2-Chloro-4,6-dimethoxypyridine. Colorless prisms, mp 81—83 °C (pentane). *Anal.* Calcd for $C_7H_8ClNO_2$: C, 48.43; H, 4.65; Cl, 20.42; N, 8.07. Found: C, 48.52; H, 4.50; Cl, 20.40; N, 8.03. ^{1}H-NMR ($CDCl_3$) δ: 3.80 (3H, s), 3.90 (3H, s), 6.13 (1H, d, $J=2$ Hz), 6.52 (1H, d, $J=2$ Hz).

6-Chloro-4-methoxypyridin-2(1*H*)-one (18)——A solution of 2-chloro-4,6-dimethoxypyridine (867 mg) in dioxane (5 ml) containing conc. HCl (10 ml) was refluxed for 4 h. The solvent was evaporated off and the residue, after being basified by the addition of aq. Na_2CO_3, was taken up in 5% MeOH–CH_2Cl_2. The organic layer was dried over $MgSO_4$. The residue obtained by evaporation of the solvent was recrystallized from ethyl acetate to give 359 mg (45%) of **18**. Colorless prisms, mp 190—194 °C (ethyl acetate). *Anal.* Calcd for $C_6H_6ClNO_2$: C, 45.16; H, 3.79; Cl, 22.22; N, 8.78. Found: C, 45.16; H, 3.98; Cl, 22.21; N, 8.49. IR (KBr): 3400, 1640 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 3.80 (3H, s), 6.10 (1H, d, $J=1.5$ Hz), 6.50 (1H, d, $J=1.5$ Hz), 11.4 (1H, br s).

2-Benzyloxy-4,6-dimethoxypyridine——A solution of 2-chloro-4,6-dimethoxypyridine (174 mg, 1 mmol) in $C_6H_5CH_2ONa/C_6H_5CH_2OH$ (prepared from 28 mg of Na and 2 ml of benzyl alcohol) was heated at 120 °C for 1.5 h. The solvent was evaporated off and the residue, after addition of water, was taken up in CH_2Cl_2. The organic layer was washed with water and dried over Na_2SO_4. The solvent was evaporated off and the residue was chromatographed on silica gel. Elution with hexane–CH_2Cl_2 (3 : 1, v/v) gave 105 mg (43%) of 2-benzyloxy-4,6-dimethoxypyridine. Colorless oil. High-resolution MS *m/z*: M$^+$ Calcd for $C_{14}H_{15}NO_3$: 245.1051. Found: 245.1081. ^{1}H-NMR ($CDCl_3$) δ: 3.73 (3H, s), 3.80 (3H, s), 5.27 (2H, s), 5.75 (1H, d, $J=1.5$ Hz), 5.80 (1H, d, $J=1.5$ Hz), 7.0—7.5 (5H, m).

4,6-Dimethoxypyridin-2(1*H*)-one (19)——A solution of 2-benzyloxy-4,6-dimethoxypyridine (700 mg, 2.9 mmol) and 10% Pd–C (100 mg) in methanol (15 ml) was hydrogenated in an atmosphere of hydrogen for 1 h. The catalyst was filtered off and the filtrate was evaporated. The residue was recrystallized from ethyl acetate to give 390 mg (87%) of **19**. Colorless prisms, mp 158—160 °C (ethyl acetate). *Anal.* Calcd for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.03. Found: C, 53.99; H, 5.88; N, 8.83. IR (KBr): 3500, 1650 cm^{-1}. ^{1}H-NMR (DMSO-d_6) δ: 3.75 (3H, s), 3.80 (3H, s), 5.68 (2H, s), 10.8 (1H, br s).

6-Methoxypyridin-2(1*H*)-one (17)——The compound was prepared from 2,6-dichloropyridine (**15**) in three steps (i—iii). i) Formation of 2-Chloro-6-methoxypyridine: A solution of **15** (14.8 g, 0.1 mol) in NaOMe/MeOH [prepared from 6.9 g (0.3 mol) of Na and methanol (150 ml)] was refluxed for 5 h. The solvent was evaporated off and the residue, after additon of water, was extracted with CH_2Cl_2. The organic layer was washed with water and dried over Na_2SO_4. Evaporation of the solvent afforded 12.0 g (84%) of 2-chloro-6-methoxypyridine. ^{1}H-NMR ($CDCl_3$) δ: 3.95 (3H, s), 6.60 (1H, d, $J=8$ Hz), 6.85 (1H, d, $J=8$ Hz), 7.50 (1H, t, $J=8$ Hz). Due to its tendency to sublime, the compound was used in the next reaction without further purification.

ii) Formation of 2-Benzyloxy-6-methoxypyridine: A solution of the crude 2-chloro-6-methoxypyridine (6.5 g, 0.045 mol) obtained above in $C_6H_5CH_2ONa$/benzyl alcohol [prepared from 1.15 g (0.05 mol) of Na and benzyl alcohol (20 ml)] was heated at 120 °C for 1 h. The solvent was evaporated off and the residue, after addition of water, was extracted with CH_2Cl_2. The organic layer was washed with water and dried over Na_2SO_4. The residue obtained after evaporation of the solvent was chromatographed on silica gel (hexane–CH_2Cl_2, 4 : 1, v/v) to give 4.8 g (50%) of 2-benzyloxy-6-methoxypyridine. Colorless oil. High-resolution MS *m/z*: M^+ Calcd.for $C_{13}H_{13}NO_2$: 215.0946. Found: 215.0936. ^{1}H-NMR ($CDCl_3$) δ: 3.90 (3H, s), 5.35 (2H, s), 6.27 (1H, d, $J=8$ Hz), 6.33 (1H, d, $J=8$ Hz), 7.0—7.5 (5H, m), 7.48 (1H, t, $J=8$ Hz).

iii) Formation of **17**: A solution of 2-benzyloxy-6-methoxypyridine (645 mg) and 10% Pd–C (100 mg) in methanol (15 ml) was hydrogenated in an atmosphere of hydrogen for 1 h. The catalyst was filtered off and the filtrate was evaporated. The residue was recrystallized from benzene–hexane to give 280 mg (75%) of **17**. Colorless needles, mp 101—103 °C (lit.[12]) mp 102—104 °C). ^{1}H-NMR ($CDCl_3$) δ: 3.83 (3H, s), 5.70 (1H, d, $J=8$ Hz), 6.25 (1H, d, $J=8$ Hz), 7.45 (1H, t, $J=8$ Hz), 9.30 (1H, br s).

General Procedure for the Synthesis of 1-(ω-Alkenyl)pyridin-2(1*H*)-ones (22—27)——Synthesis of 1-(3-Butenyl)-4,6-dimethoxypyridin-2(1*H*)-one (**25**: $n=2$) as a Typical Example: Finely powdered KOH (1.68 g, 30 mmol) and $(n\text{-}Bu)_4N^+HSO_4^-$ (0.34 g, 1 mmol) were added to a solution of **19** (0.47 g, 3 mmol) in benzene (50 ml). Under stirring, 4-bromo-1-butene (1.35 g, 10 mmol) was added to the 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 water and dried over Na_2SO_4. The residue obtained by evaporation of the solvent was chromatographed on silica gel. Elution with hexane–CH_2Cl_2 (5 : 1, v/v) gave 2-(3-butenyloxy)-4,6-dimethoxypyridine (**31**: $n=2$). Elution with CH_2Cl_2 gave 0.11 g (18%) of **25** ($n=2$) (Table I).

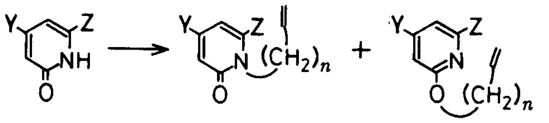
25 ($n=2$). Colorless oil. UV λ_{max} (MeOH) nm: 283. IR ($CHCl_3$): 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.0—2.6 (2H, m), 3.73 (3H, s), 3.80 (3H, s), 4.06 (2H, t, $J=7$ Hz), 4.8—5.3 (2H, m), 5.28 (1H, d, $J=2$ Hz), 5.58 (1H, d, $J=2$ Hz), 5.5—6.1 (1H, m).

31 ($n=2$). Colorless oil. UV λ_{max} (MeOH) nm: 226, 263. IR ($CHCl_3$): 1610 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.3—2.8 (2H, m), 3.80 (3H, s), 3.90 (3H, s), 4.30 (2H, t, $J=7$ Hz), 5.0—5.4 (2H, m), 5.6—6.2 (1H, m), 5.90 (2H, s).

The following compounds were prepared in the same manner, and the results are shown in Table I. The structures of these compounds are supported by acceptable UV, IR, and NMR data. In all cases, the *N*-alkenylated products were more polar than the *O*-alkenylated products.

General Procedure for Photochemical Synthesis of the Parallel Adducts (36—38) from 1-(ω-Alkenyl)pyridin-

TABLE I. Reactions of 2-Pyridones with ω-Alkenyl Bromides



22—27[a)] **28—33**[b)]

Y	Z	*n*	Formula	M^+ Calcd *m/z*[c)]	Compd. No.	Yield (%)	M^+ Found *m/z*[c)]	Compd. No.	Yield (%)	M^+ Found *m/z*[c)]
H	H	3	$C_{10}H_{13}NO$	163.0996	**27**	82	163.0993	**33**	13	163.0990
OMe	H	2	$C_{10}H_{13}NO_2$	179.0946	**26**	69	179.0950	**32**	9	179.0947
OMe	H	3	$C_{11}H_{15}NO_2$	193.1102	**26**	91	193.1118	**32**	0	—
H	Cl	2	$C_9H_{10}ClNO$	183.0450 185.0422	**22**	15	183.0446 185.0432	**28**	65	183.0448 185.0432
H	Cl	3	$C_{10}H_{12}ClNO$	197.0607 199.0578	**22**	23	197.0617 199.0591	**28**	71	197.0597 199.0572
H	Cl	4	$C_{11}H_{14}ClNO$	211.0763 213.0733	**22**	23	211.0748 213.0718	**28**	68	211.0747 213.0730
H	OMe	2	$C_{10}H_{13}NO_2$	179.0946	**24**	16	179.0952	**30**	62	179.0944
H	OMe	3	$C_{11}H_{15}NO_2$	193.1102	**24**	22	193.1093	**30**	70	193.1102
OMe	Cl	3	$C_{11}H_{14}ClNO$	227.0712 229.0684	**23**	18	227.0729 229.0692	**29**	68	227.0700 229.0708
OMe	OMe	2	$C_{11}H_{15}NO_2$	209.1051	**25**	18	209.1063	**31**	69	209.1058
OMe	OMe	3	$C_{12}H_{17}NO_3$	223.1207	**25**	23	223.1208	**31**	70	223.1207
OMe	OMe	4	$C_{13}H_{19}NO_3$	237.1364	**25**	22	237.1364	**31**	69	237.1369

a) 1-(ω-Alkenyl)pyridin-2(1*H*)-ones. *b*) 2-(ω-Alkenyloxy)pyridines. *c*) *m/z* (upper column) corresponds to ^{35}Cl; *m/z* (lower column) corresponds to ^{37}Cl.

2(1*H*)-ones (24—26)——Synthesis of 7,7b-Dimethoxy-5-oxo-1a,2,3,5,7a,7b-hexahydro-1*H*-cyclobuta[*hi*]indolizine (**37**: $n=2$) as a Typical Example: A solution of **25** ($n=2$, 42 mg, 0.2 mmol) in acetone (40 ml) was irradiated at 300 nm for 30 min. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with ether gave 29 mg (69%) of **37** ($n=2$).

37 ($n=2$). Colorless prisms, mp 113—115 °C (pentane). High-resolution MS *m*/*z*: M^+ Calcd for $C_{11}H_{15}NO_3$: 209.1051. Found: 209.1030. UV λ_{max} (MeOH) nm: 216, 252. IR ($CHCl_3$): 1635 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.05—1.4 (1H, m), 1.5—1.9 (1H, m), 2.0—2.4 (1H, m), 2.4—3.0 (3H, m), 3.20 (3H, s), 3.37 (1H, dt, $J=9$, 12 Hz), 3.64 (3H, s), 4.28 (1H, ddd, $J=3$, 9, 12 Hz), 5.05 (1H, s).

The following compounds were prepared in the same manner.

2,8b-Dimethoxy-4-oxo-1a,6,7,8,8a,8b-hexahydro-1*H*,4*H*-cyclobuta[*ij*]quinolizine (**37**: $n=3$). Yield: 72%. Colorless prisms, mp 122—124 °C (pentane). High-resolution MS *m*/*z*: M^+ Calcd for $C_{12}H_{17}NO_3$: 223.1207. Found: 223.1194. UV λ_{max} (MeOH) nm (log ε): 217 (4.00), 250 (3.71). IR ($CHCl_3$): 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$): 1.2—1.95 (5H, m), 2.20 (1H, dt, $J=9$, 10 Hz), 2.4—2.8 (2H, m), 2.80 (1H, t, $J=9$ Hz), 3.10 (3H, s), 3.62 (3H, s), 4.2—4.45 (1H, m), 5.07 (1H, s).

7b-Methoxy-5-oxo-1a,2,3,5,7a,7b-hexahydro-1*H*-cyclobuta[*hi*]indolizine (**36**: $n=2$). Yield: 47%. Colorless prisms, mp 44—46 °C (ether–pentane). High-resolution MS *m*/*z*: M^+ Calcd for $C_{10}H_{13}NO_2$: 179.0946. Found: 179.0962. UV λ_{max} (MeOH) nm: 212, 250 (sh). IR ($CHCl_3$): 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.0—1.35 (1H, m), 1.5—1.75 (1H, m), 2.0—2.35 (1H, m), 2.4—3.0 (3H, m), 3.20 (3H, s), 3.35 (1H, dt, $J=9$, 12 Hz), 4.35 (1H, ddd, $J=$ 3, 9, 12 Hz, 5.92 (1H, d, $J=10$ Hz), 6.52 (1H, dd, $J=6$, 10 Hz).

8b-Methoxy-4-oxo-1a,6,7,8,8a,8b-hexahydro-1*H*,4*H*-cyclobuta[*ij*]quinolizine (**36**: $n=3$). Yield: 45%. Colorless prisms, mp 58—60 °C (ether–pentane). High-resolution MS *m*/*z*: M^+ Calcd for $C_{11}H_{15}NO_2$: 193.1102. Found: 193.1114. UV λ_{max} (MeOH) nm: 211, 250 sh. IR ($CHCl_3$): 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.0—2.0 (5H, m), 2.0—2.3 (1H, m), 2.4—2.9 (3H, m), 3.12 (3H, s), 4.2—4.3 (1H, m), 5.88 (1H, d, $J=10$ Hz), 6.52 (1H, dd, $J=6$, 10 Hz).

7-Methoxy-5-oxo-1a,2,3,5,7a,7b-hexahydro-1*H*-cyclobuta[*hi*]indolizine (**38**: $n=2$). Yield: 59%. Colorless prisms, mp 52—55 °C (ether–pentane). High-resolution MS *m*/*z*: M^+ Calcd for $C_{10}H_{13}NO_2$: 179.0946. Found: 179.0967. UV λ_{max} (MeOH) nm: 215, 262. IR ($CHCl_3$): 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.5—2.2 (3H, m), 2.5—3.0 (3H, m), 3.04 (1H, dt, $J=9$, 12 Hz), 3.60 (3H, s), 4.05 (1H, dt, $J=4$, 5 Hz), 4.18 (1H, ddd, $J=3$, 9, 12 Hz), 5.0 (1H, s).

2-Methoxy-4-oxo-1a,6,7,8,8a,8b-hexahydro-1*H*,4*H*-cyclobuta[*ij*]quinolizine (**38**: $n=3$). Yield: 41%. Colorless oil. High-resolution MS *m*/*z*: M^+ Calcd for $C_{11}H_{15}NO_2$: 193.1102. Found: 193.1103. UV λ_{max} (MeOH) nm: 214, 260. IR ($CHCl_3$): 1645 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.5—1.9 (4H, m), 2.05—3.0 (5H, m), 3.60 (3H, s), 3.85—4.1 (1H, m), 4.35—4.7 (1H, m), 5.0 (1H, s).

The corresponding parallel adduct (**39**: $n=3$) could not be obtained by photolysis of 1-(4-pentenyl)pyridin 2-(1*H*)-one (**27**: $n=3$) under the same conditions.

General Procedure for Photochemical Conversion of 6-Chloro-1-(ω-alkenyl)pyridin-2(1*H*)-ones (22 and 23) to the Cyclized Products (34 and 35)——Formation of 9-Chloromethyl-4-oxo-6,7,8,9-tetrahydro-4*H*-quinolizine (**34**: $n=3$) as a Typical Example: A solution of **22** ($n=3$, 198 mg, 1 mmol) in acetone (300 ml) was irradiated at 300 nm for 1 h. After evaporation of the solvent, the residue was chromatographed on silica gel. Elution with 1% MeOH–CH_2Cl_2 gave 36 mg (18%) of **34** ($n=3$). Colorless prisms, mp 88—90 °C (hexane–ether). High-resolution MS *m*/*z*: M^+ Calcd for $C_{10}H_{12}ClNO$: 197.0607 (^{35}Cl) and 199.0578 (^{37}Cl). Found: 197.0618 and 199.0578. IR ($CHCl_3$): 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.2—2.45 (4H, m), 3.0—3.3 (1H, m), 3.5—4.4 (4H, m), 6.0—6.2 (1H, m), 6.3—6.6 (1H, m), 7.25 (1H, dd, $J=7$, 9 Hz).

When the above irradiation reaction was carried out using acetone (300 ml) containing 1 ml of conc. HCl, the yield of the product was increased to 83 mg (42%).

The following compounds were prepared in the same manner.

1-Chloromethyl-5-oxo-1,2,3,5-tetrahydroindolizine (**34**: $n=2$). Yield: 7% (MeOH) and 13% (HCl–MeOH). Colorless prisms, mp 141—143 °C (ether–hexane). High-resolution MS *m*/*z*: M^+ Calcd for $C_9H_{10}ClNO$: 183.0450 (^{35}Cl) and 185.0422 (^{37}Cl). Found: 183.0453 and 185.0432. IR ($CHCl_3$): 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.8—2.65 (2H, m), 3.5—3.9 (3H, m), 3.9—4.45 (2H, m), 6.16 (1H, d, $J=6$ Hz), 6.44 (1H, d, $J=8$ Hz), 7.35 (1H, dd, $J=6$, 8 Hz).

9-Chloromethyl-2-methoxy-4-oxo-6,7,8,9-tetrahydro-4*H*-quinolizine (**35**: $n=3$). Yield: 15% (MeOH). Colorless prisms, mp 110—112 °C (ether–pentane). High-resolution MS *m*/*z*: M^+ Calcd for $C_{11}H_{14}ClNO_2$: 227.0712 (^{35}Cl) and 229.0683 (^{37}Cl). Found: 227.0719 and 229.0693. IR ($CHCl_3$): 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.6—2.2 (4H, m), 2.9—3.25 (1H, m), 3.4—4.6 (4H, m), 7.84 (2H, s). The corresponding cyclized product (**34**: $n=4$) could not be obtained by irradiation of 6-chloro-1-(5-hexenyl)pyridin-2(1*H*)-one (**22**: $n=4$) under the same conditions.

Reaction of the Parallel Adducts (36 and 37) with Stannic Chloride——Formation of **35** ($n=3$) from the Adduct (**37**: $n=3$) as a Typical Example: Stannic chloride (0.1 ml) was added to a solution of the adduct (**37**: $n=3$, 0.155 mmol) in benzene (1 ml) and the whole was kept standing overnight. After addition of ice-water and basification with K_2CO_3, the product was extracted with CH_2Cl_2. The organic layer was washed with water and dried over Na_2SO_4. The residue obtained after evaporation of the solvent was subjected to PTLC (2% MeOH–CH_2Cl_2) to give 6 mg (33%) of **35** ($n=3$).

The following compounds were obtained in the same manner.

1-Chloromethyl-7-methoxy-5-oxo-1,2,3,5-tetrahydroindolizine (**35**, $n=2$). Yield: 7 mg (22%). Colorless prisms, mp 101—103 °C (ether–pentane). High-resolution MS *m/z*: M^+ Calcd for $C_{10}H_{12}ClNO_2$: 213.0556 (^{35}Cl) and 215.0525 (^{37}Cl). Found: 213.0510 and 215.0520. IR ($CHCl_3$): 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.7—2.65 (2H, m), 3.4—4.3 (5H, m), 5.75—6.0 (2H, m).

34 ($n=2$). Yield: 17%.

4,6-Dimethoxy-1-methylpyridin-2(1*H*)-one (42)——A mixture of 2,4,6-trimethoxypyridine (761 mg, 4.5 mmol) and MeI (7 g, 50 mmol) was heated in a sealed tube at 90 °C for 12 h. The excess of MeI was evaporated off and the residue was chromatographed on silica gel with 2% MeOH–CH_2Cl_2 to give **42**. Yield: 637 mg (84%). Colorless prisms, mp 92—94 °C (ether–hexane). *Anal.* Calcd for $C_8H_{11}NO_3$: C, 56.79; H, 6.55; N, 8.28. Found: C, 56.81; H, 6.49; N, 8.28. IR ($CHCl_3$): 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.40 (3H, s), 3.77 (3H, s), 3.87 (3H, s), 5.25 (1H, d, $J=3$ Hz), 5.65 (1H, d, $J=3$ Hz). MS *m/z*: 169 (M^+).

1,5-Dimethoxy-2-methyl-3-oxo-2-azabicyclo[4.2.0]oct-4-ene (43)——A solution of **42** (169 mg, 1 mmol) in acetone (140 ml) was irradiated at ≥300 nm under bubbling of ethylene for 6 h. The solvent was evaporated off and the residue was chromatographed on silica gel. Elution with ether gave 23 mg (15%) of *N*-methyl-3-methoxyglutaconimide. Colorless prisms, mp 115—115.5 °C (ether–hexane). High-resolution MS *m/z*: M^+ Calcd for $C_7H_9NO_3$: 155.0582. Found: 155.0547. IR ($CHCl_3$): 1708, 1663, 1633 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 3.23 (3H, s), 3.46 (2H, s), 3.80 (3H, s), 5.46 (1H, s).

Elution with 1% MeOH–CH_2Cl_2 gave 15 mg (9%) of **43** and then 25 mg (15%) of the starting material (**42**).

43. Colorless prisms, mp 75—77 °C (pentane). High-resolution MS *m/z*: M^+ Calcd for $C_{10}H_{15}NO_3$: 197.1051. Found: 197.1048. UV λ_{max} (MeOH) nm (log ε): 215 (4.06), 243 (3.76). IR ($CHCl_3$): 1645, 1610 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.0—2.5 (4H, m), 2.82 (3H, s), 2.9—3.1 (1H, m), 3.02 (3H, s), 3.64 (3H, s), 5.08 (1H, s). The UV spectrum of **43** closely resembled that of **37** ($n=3$).

6-Methoxy-4-oxo-3-methyl-1,2,3,4-tetrahydrocyclobuta[*b*]pyridine (44)——A solution of **43** (7.0 mg, 0.036 mmol) in benzene (2 ml) containing *tert*-BuOK (33 mg, 0.3 mmol) was refluxed for 0.5 h. After the addition of CH_2Cl_2, the organic layer was washed with water and dried (Na_2SO_4). The solvent was evaporated off and the residue was recrystallized from CH_2Cl_2–hexane to give **44**. Yield: 4.3 mg (72%). Colorless prisms, mp 139—140 °C. High-resolution MS *m/z*: M^+ Calcd for $C_9H_{11}NO_2$: 165.0789. Found: 165.0802. UV λ_{max} (MeOH) nm: 210, 228 (sh), 295. IR ($CHCl_3$): 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 2.88 (2H, t, $J=3.5$ Hz), 3.10 (2H, t, $J=3.5$ Hz), 3.28 (3H, s), 3.76 (3H, s), 5.76 (1H, s).

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References and Notes

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14) Due to the low solubility of 4,6-dimethoxypyridin-2(1*H*)-one (**19**) in acetone, its 1-methyl derivative (**42**) was

used.

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