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Photoaddition of 2-Quinolone and 2-Pyridone Derivatives to Diketene: On the Regioselectivity of the Photoaddition[1,2]

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Photoaddition of 2-pyridones and 2-quinolones to diketene or allene gave the head-to-tail adducts, irrespective of the kind of 4-substituent. Therefore, the adducts obtained by the photoaddition of 2-quinolone, 4-methyl-2-quinolone, and their 1-methyl derivatives to diketene (previously assigned as having the head-to-head structure) have now been determined to have the head-to-tail structure. The stereochemistry of the adducts derived from these 2-quinolones and diketene was determined by X-ray crystallographic analysis and nuclear magnetic resonance spectroscopy.

Keywords——diketene; allene; photoaddition; [2+2] cycloaddition; X-ray analysis; regioselectivity; spirooxetanone; 1-methylene-1,2-dihydrocyclobuta[*c*]quinoline; stereochemisty

Kaneko, Naito, and their collaborators have demonstrated that 4-methoxy-2-quinolone and its 1-methyl derivative readily undergo photoaddition to a series of olefins.[3] The yields of the photoadducts are very high due to an inability of 4-methoxy-2-quinolones to photodimerize. Though the presence of methyl substituents at the 3- and/or 4-position of 2-quinolone derivatives also hindered the dimerization reaction, these quinolones[4] as well as 2-quinolone itself[5] still undergo efficient photoaddition to olefins. One of the characteristic features of this photoaddition reaction is the regioselectivity; only the head-to-tail adducts are formed.[6] Thus, irrespective of the kind of olefins, 2-quinolone[6] and 4-methyl-,[7] 4-hydroxy-,[8] and 4-methoxy-2-quinolones[3,9] all gave the head-to-tail adducts, regioselectively. The only exception is the photoaddition of 4-methoxy-1-methyl-2-quinolone to allene giving the head-to-head adduct, though the major product is again the head-to-tail adduct.[10]

In their continuing study of photoreactions between diketene and olefinic compounds,[11] Chiba, Kato, and their collaborators recently examined the photoaddition of 2-quinolone derivatives to diketene and reached the conclusion that though 4-acetoxy-2-quinolone afforded the head-to-tail adducts, the adducts obtained from 2-quinolone and its 4-methyl

derivative had the head-to-head structure.[12] However, as mentioned above, selective formation of the head-to-head adducts had never previously been observed in the photoaddition of 2-quinolones to alkenes. Furthermore, the assignment of the head-to-head structure for these adducts rested entirely upon nuclear magnetic resonance (NMR) spectroscopy and hence was not definitive. For these reasons, we decided to reinvestigate the photoaddition of 2-quinolone and its 4-methyl derivative to diketene and after co-operative work have reached the conclusion that these adducts have the head-to-tail structure, and not the head-to-head structure as previously assigned.[12,13] This paper describes the results of this work as well as the photoaddition of 4-methoxy-2-pyridone and its derivatives to diketene. The stereochemistry of the adducts derived from these quinolones and diketene was determined by X-ray crystallographic analysis and NMR spectroscopy.

Verification of the Head-to-Tail Structure for the Adducts Obtained by Photoaddition of 1-Methylquinolin-2(1*H*)-one to Diketene

Chiba *et al.* reported that the photoreaction of diketene with 1-methyl-2-quinolone (**1a**) gave [2+2] adducts (**4'a**: as two diastereoisomers), which were transformed by thermolysis to the methylene cyclobuta[*c*]quinolone (**5'a**).[12] Later, they found that treatment of **5'a** with sodium ethoxide in toluene resulted in the formation of 2,4-dimethyl-1,2-dihydro-

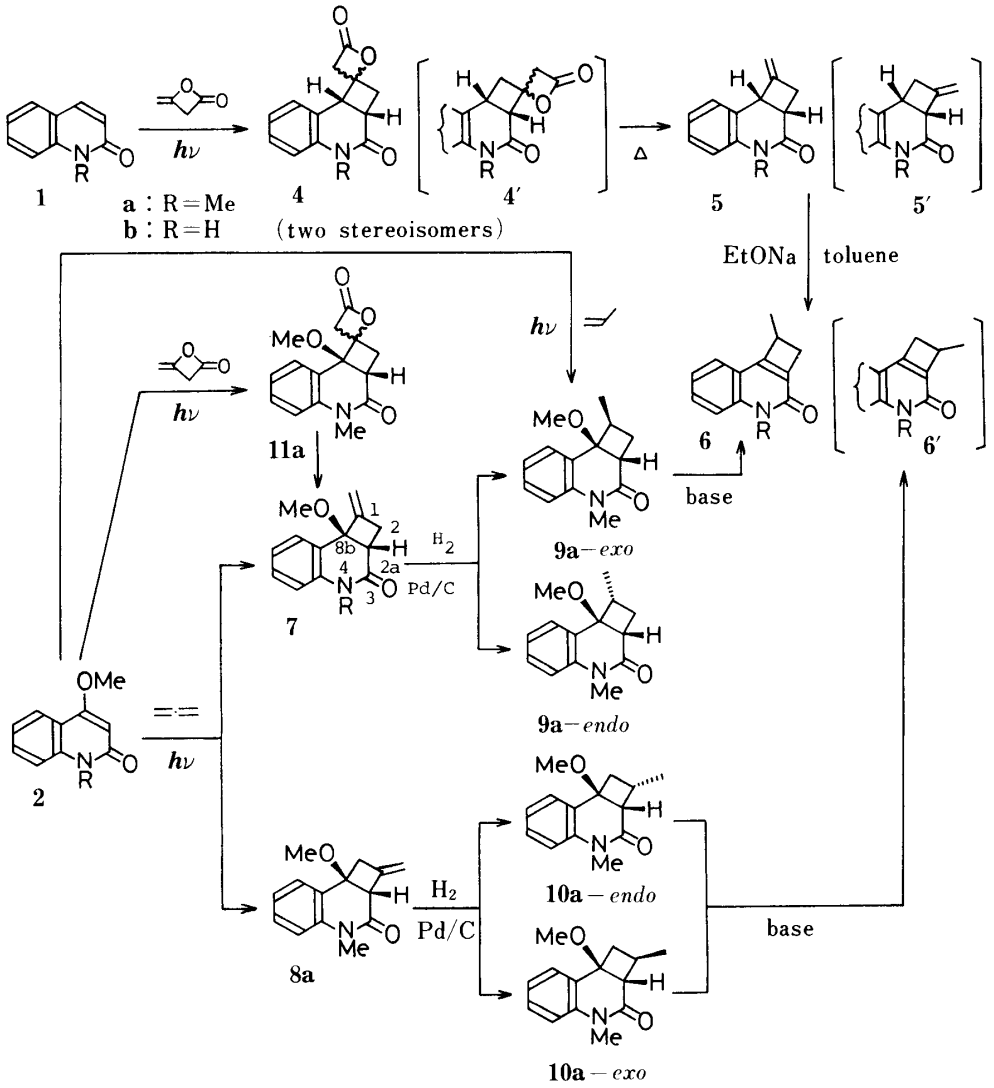


Chart 1

cyclobuta[*c*]quinolin-3(4*H*)-one (**6'a**).[13] Assignments of the structures of **5'a** and **6'a** rested entirely upon the assumption that the photoadduct (**4'a**) had the head-to-head structure. Kaneko *et al.* obtained two kinds of [2+2] adducts, **7a** and **8a**, in a ratio of *ca.* 6 : 1 by photoaddition of 4-methoxy-1-methyl-2-quinolone (**2a**) to allene.[10] Catalytic hydrogenation of the major adduct (**7a**) afforded the corresponding dihydro derivatives (**9a**) as a mixture of two separable stereoisomers. Both isomers show the 2a-proton signals in the NMR spectra as a triplet (2a-H of **9a**-*exo*, δ 3.39 and that of **9a**-*endo*, 3.20). This fact as well as the exclusive formation of **9a** (again two diastereoisomers) from photoaddition of **2a** to propene demonstrated unambiguously the head-to-tail structure for the major adduct (**7a**). The dihydro derivative (**9a**-*exo*) was treated with base to give a cyclobutene (**6a**). By a similar transformation, the minor adduct (**8a**) was converted to another cyclobutene (**6'a**). Though both cyclobutenes (**6a** and **6'a**) show almost the same NMR spectra, it is clear from the above experiments that **6a** is 1-methyl-1,2-dihydrocyclobuta[*c*]quinolin-3(4*H*)-one and **6'a** is the corresponding 2-methyl derivative. This conclusion was confirmed by comparison of the NMR spectra of the adducts (**7a** and **8a**) in which the 2a-proton signal of **8a** appears at far lower field (δ 3.94, as a broad singlet) than that (δ 3.44, t, J=9 Hz) of **7a**.

The **6**-type compound obtained by Chiba *et al.* from **1a** and diketene was identical with the compound (**6a**) derived from the major product (**7a**) obtained by photoaddition of **2a** to allene on the basis of mixed melting point determination and comparison of the infrared (IR) spectra. Hence, the structure of the photoadducts obtained from **1a** and diketene has now been determined unequivocally as the head-to-tail structure (**4a**) and not the head-to-head structure (**4'a**) as assigned previously.[12] The structure of the adduct obtained from **1b** and diketene[12] should also be revised to **4b**.

It should be noted that the photoadducts (**11a**: two diastereoisomers) obtained from 4-methoxy-1-methyl-2-quinolone (**2a**) and diketene also afforded **7a** on thermolysis. Therefore, it is evident that the photoaddition also proceeded in a regioselective manner to give only the head-to-tail adducts (**11a**).

Verification of the Head-to-Tail Structure for the Products Obtained by Photoaddition of 1,4-Dimethylquinolin-2(1*H*)-one to Diketene

Chiba *et al.* obtained two adducts by photoaddition of 1,4-dimethyl-2-quinolone (**3**) to

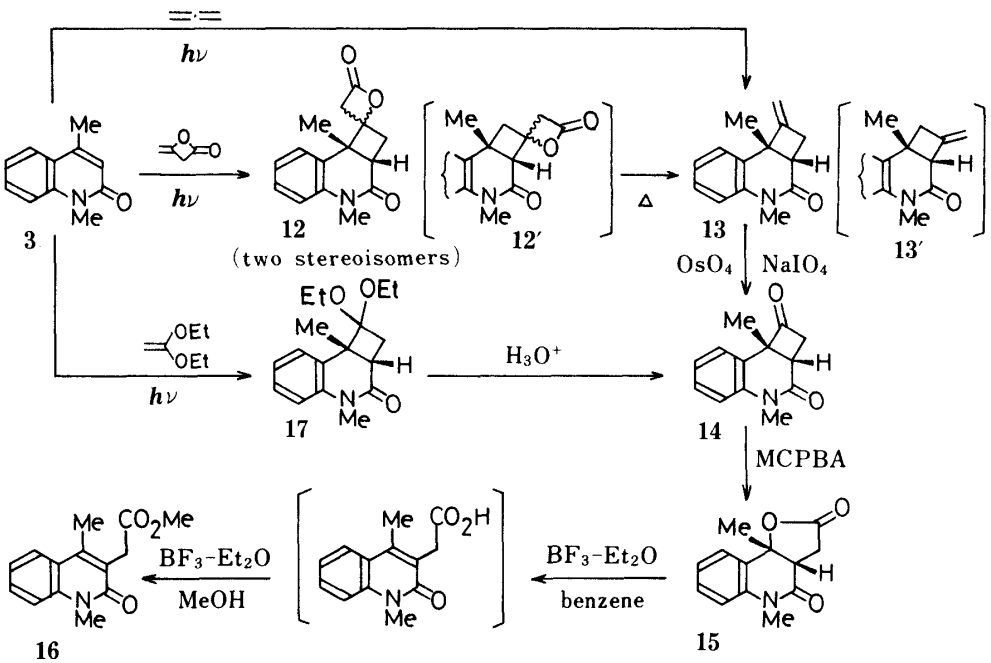


Chart 2

diketene. On thermolysis, both adducts eliminated carbon dioxide to give the corresponding methylene cyclobutane as a common product. This result indicates that the adducts are stereoisomeric. They assigned the head-to-head structure (**12'**) for these adducts.[12]

The following experiments were then carried out to determine the structure of these adducts. Thus, irradiation of **3** in methanol in the presence of an excess of allene was found to give a single adduct (**13**) as a sole product in high yield. The adduct (**13**) was identical with the methylene cyclobutane (assigned previously as **13'**) obtained by decarboxylation of the photoadducts of **3** to diketene on the basis of mixed melting point determination and comparison of the IR spectra. Oxidation of the adduct (**13**) with osmium tetroxide-periodate then afforded the ketone (**14**), which, on Baeyer–Villiger oxidation with *m*-chloroperbenzoic acid, gave the γ-lactone (**15**). The NMR spectrum of the lactone shows a doublet of doublets at δ 3.37 ($J=8$ and 12 Hz) due to the 3a-proton. Furthermore, treatment of the lactone with boron trifluoride-etherate in benzene and then with methanol gave 1-methyl-2-quinolone (**16**) having methyl and methoxycarbonylmethyl groups in the pyridone ring. Since the methyl group should be attached to the 4-position of the 2-quinolone ring, the latter group (CH_2COOMe) should be at the 3-position. Hence, the structure of the ester (**16**) is determined as 1,4-dimethyl-3-methoxycarbonylmethylquinolin-2(1*H*)-one. Consideration of the reaction sequence for the formation of **16** leads to the structures of the γ-lactone, cyclobutanone, and methylene cyclobutane as **15**, **14**, and **13**, respectively. From the above experiments, the adducts obtained by the photoaddition of **3** to diketene have now been clarified as having the head-to-tail structure (**12**).

It should be noted that photoaddition of **3** to ketene diethylacetal also afforded the head-to-tail adduct (**17**), because acid hydrolysis of the adduct gave the same cyclobutanone (**14**).

Photoaddition of 4-Methoxy-2-pyridone and Related Compounds to Diketene and Allene

Kaneko *et al.* have recently shown that photoaddition of 4-acetoxy-6-methyl-2-pyridone (**18b**) to allene in acetone affords the head-to-tail adduct (**20b**) regioselectively. Treatment of **20b** with base gave 5-methyl-1-methylene-1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one (**21**).[10] The same 1-methylene cyclobutene (**21**) was also synthesized from 4-methoxy-6-methyl-2-pyridone (**18a**) by the same two-step procedure: the Kaneko–Naito method.[9] This experiment shows that 4-oxygenated 2-pyridones add to allene *via* their triplet excited state[14] to give the head-to-tail adducts irrespective of the kind of protecting group on the 4-hydroxy function. Catalytic hydrogenation of **21** afforded the corresponding dihydro derivative (**22**). The independent synthesis of **22** by photoaddition of **18b** to propene and subsequent base treatment of the adduct (**23b**) revealed unequivocally that **22** is 1,5-dimethyl-1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one and hence the adduct (**20**) has the head-to-tail structure. The head-to-tail structure of the adduct (**23b**) was readily deduced from the appearance of the 2a-proton signal as a triplet (δ: 3.28 with $J=9.6$ Hz).

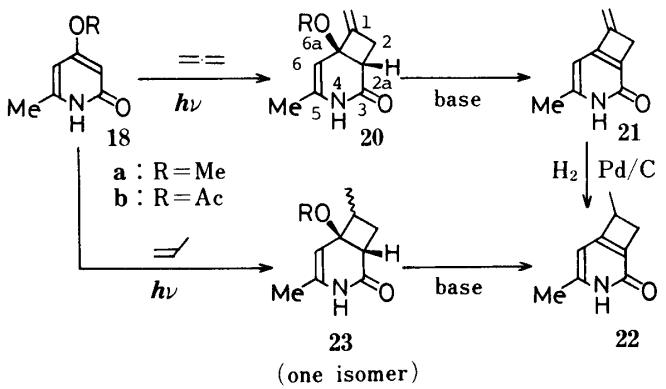


Chart 3

As mentioned in the foregoing sections, the methylene cyclobutanes (*e.g.*, **20**) can also be synthesized by thermolytic elimination of carbon dioxide from the adduct obtained from 2-pyridones and diketene. Therefore, the regioselectivity in the photoaddition reactions of 2-pyridones to diketene can be checked simply by comparison of the methylene cyclobutanes obtained by the two routes using either allene or diketene as the counterpart of the photoaddition step. Namely, if the methylene cyclobutanes from both routes are the same, one can conclude that diketene gives the head-to-tail adduct, and if they are not the same, the head-to-head adduct.

Based on this assumption, we carried out the following experiments. Thus, 4-methoxy-1-methyl-2-pyridone (**19a**) was irradiated in acetone in the presence of diketene to give a separable mixture of two diastereoisomers (**24a**). On heating, both isomers afforded a methylene cyclobutane (**25a**) as a common product. The fact that the same cyclobutane (**25a**) was also formed directly by photoaddition of **19a** to allene shows that photoaddition of **19a** to diketene proceeded regioselectively to give the head-to-tail adduct (**24a**).

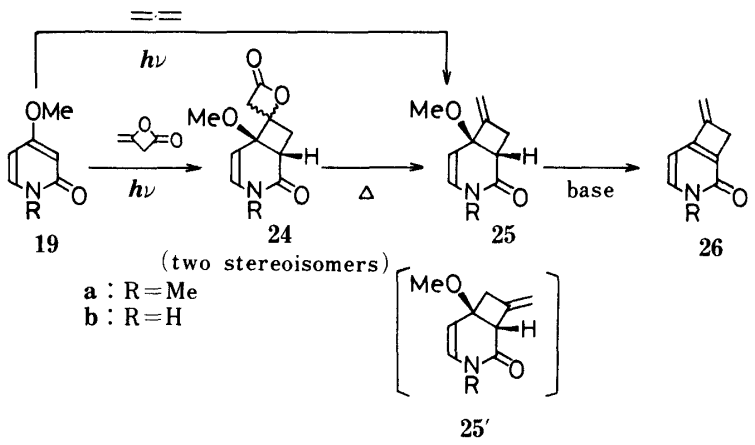


Chart 4

This conclusion is also supported by the fact that the NMR spectrum of the methylene cyclobutane (**25a**) shows no signal around δ 4.0 due to the 2a-proton (expected for the isomeric 2-methylene cyclobutane structure, **25′**).

1-Methylene-1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one (**26b**) and its 4-methyl derivative (**26a**) were synthesized from either **19b** or **19a** as shown in Chart 4.

Stereochemistry of the Adducts Formed by Photoaddition of 2-Quinolones to Diketene and Determination of Stereostructure of *exo*-Isomer of 4-Methyl-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one-1-spiro-2′-(oxetan)-4′-one by X-Ray Crystallographic Analysis

As mentioned in foregoing sections, the photoadducts of 2-quinolones to diketene were determined as having the head-to-tail structure from purely chemical considerations. In order to confirm the above conclusion as well as to clarify the stereochemistry of these adducts, X-ray analysis of **4a** (mp 138—139 °C) was carried out. A projection of the molecular structure thus obtained is shown in Fig. 1. Figure 1 also includes the numbering of the atoms and rings of **4a**.

The bond lengths and angles of **4a** (mp 138—139 °C) are shown in Fig. 2.

As shown in Table I, rings A and B are almost planar and the dihedral angles between the least-squares planes of rings A-B and C and rings C and D are *ca.* 64 ° and 90 °, respectively.

The molecular structure of **4a** (mp 138—139 °C) thus determined not only confirms its head-to-tail structure, but also shows that **4a** is the *exo*-isomer. Hereafter, we define the stereochemistry of these adducts as *exo* (benzene ring and oxetane oxygen atom are in a *trans*-

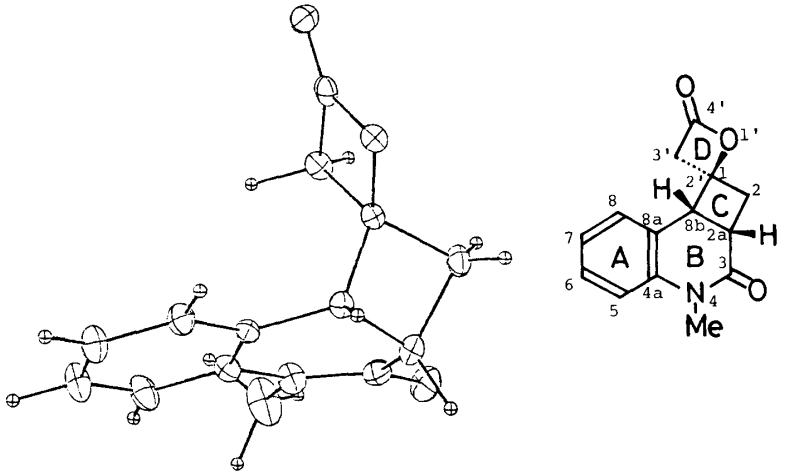
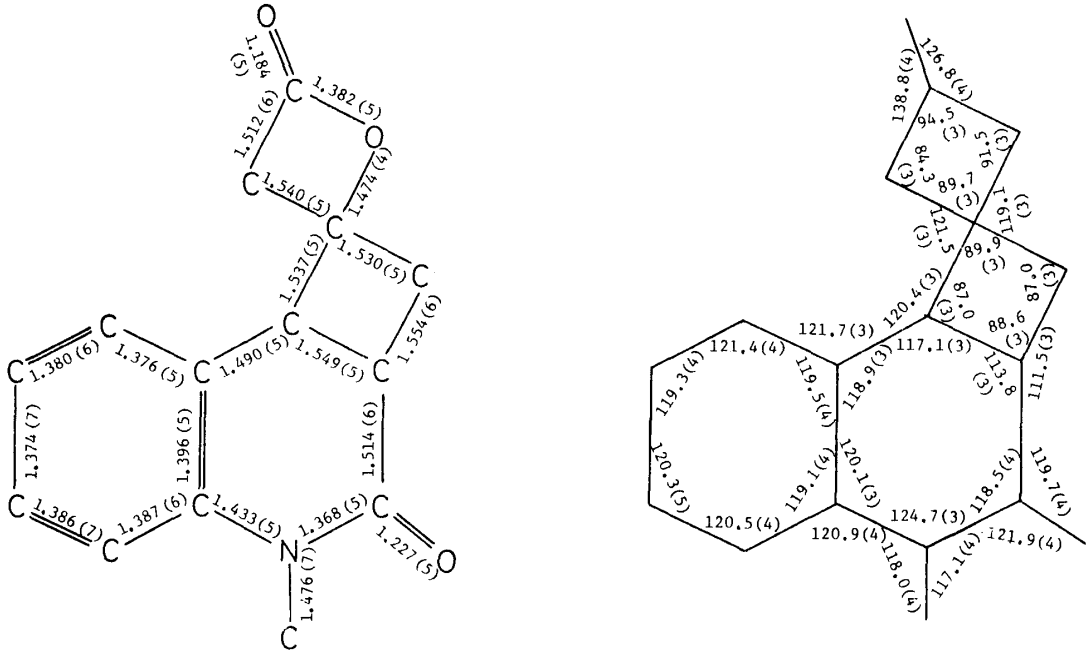


Fig. 1. Molecular Structure and Numbering of the Atoms and Rings of **4a**-*exo* (mp 138—139 °C)



$\angle C_2$–C_1–$C_{3'}$ 121.4 (3)
$\angle C_{8b}$–C_1–$O_{1'}$ 118.5 (3)

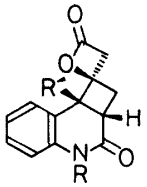
Fig. 2. Bond Lengths (Å) and Angles (°) of **4a**-*exo*

relationship on the cyclobutane ring) and *endo* (these two functions are in *cis*-relationship) on the above basis. Since **4a**-*exo* (mp 138—139 °C) and **4a** (mp 163—164.5 °C) are diastereoisomeric (*vide ante*), the stereochemistry of **4a** (mp 163—164.5 °C) is automatically determined as *endo*. Assignment of *endo*- and *exo*-structures is also possible from NMR spectra. A typical difference between the spectra of **4a**-*exo* and **4a**-*endo* is the chemical shift of one of the methylene protons ($C_{3'}$–H), namely, the one in **4a**-*exo* appears at higher field (δ 2.95 d, J= 16 Hz) than those (δ 3.52 s, 2 protons) in **4a**-*endo*. This is because shielding (up-field shift) of $C_{3'}$–H by the benzene ring is only possible for the adduct having a *cis*-relationship between these two groups. By analogy, the adducts showing signals at δ 2.95 (**11a**-*exo*, mp 138—

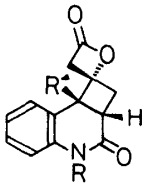
TABLE I. Dihedral Angles between the Least-Squares Planes of **4a**-*exo*

A-Ring–B-ring	9°	C-Ring–D-ring	90°
A-Ring–C-ring	62°	A+B-Ring–A-ring	4°
A-Ring–D-ring	75°	A+B-Ring–B-ring	5°
B-Ring–C-ring	66°	A+B-Ring–C-ring	64°
B-Ring–D-ring	67°	A+B-Ring–D-ring	72°

140 °C) and δ 2.98 (12-*exo*, mp 131—132 °C) are assigned as the *exo*-isomers, and the other adducts (**11a**-*endo*, mp 163—164.5 °C and **12**-*endo*, mp 176—177.5 °C) as the *endo*-isomers. It should be noted that addition of 2-quinolones to diketene always affords an *exo*-isomer predominantly.



exo isomer



endo isomer

	R	R′
4a	Me	H
4b	H	H
11a	Me	OMe
12	Me	Me

Chart 5

Since such shielding by the benzene ring also exists at the 1-methyl group in the **9**-type compounds so long as these two groups are in a *cis*-relationship on the cyclobutane ring, our previous assignment[10] for these compounds (**9**-*exo* and 9-*endo*) has now gained strong support.

The stereochemistry of **10a** (one isomer shows 2-methyl signal at δ 0.86 and the other at δ 1.26) is also assignable on the basis of the spectra. Only the 2-methyl group in **10a**-*endo* would be shielded by the carbonyl group.[10]

Conclusions

The present study has shown that photoaddition of 2-quinolones and 2-pyridones to diketene proceeds regioselectively to give only the head-to-tail adducts, just as in the photoaddition to an ordinary olefin. The same regioselectivity also exists in the photoaddition with allene or ketene diethylacetal instead of diketene. Furthermore, the *endo*- and *exo*-configurations of the adducts formed by the addition of 2-quinolones to diketene were determined.

Hence, the previously proposed head-to-head structures for some adducts formed from 2-quinolones and diketene (**4′a**, **4′b**, **12′**) should be revised to the corresponding head-to-tail structures (**4a**, **4b**, **12**), respectively.

Experimental

All melting points were determined on a micro-hot stage (Yanagimoto) and are uncorrected. IR were recorded on a Shimadzu IR-420 spectrometer, ultraviolet (UV) spectra with a Hitachi 320 spectrometer, and NMR spectra on a JEOL JNM-60 or JEOL JNM-FX-100 spectrometer (with tetramethylsilane as an internal standard). Mass spectra (MS) were taken either with a Hitachi M-80 spectrometer or with a JEOL JMS-01SG-2 spectrometer.

Photolyses were carried out in a Pyrex immersion apparatus equipped with an Ushio 450W or Toshiba 400P high-pressure mercury lamp (this corresponds to irradiation at $\geq$ 300 nm) cooled internally with running water.

Silica gel used for column chromatography was 100—200 mesh, purchased from Kanto Chemical Co., Inc.

Preparative thin-layer chromatography (PTLC) was performed on Merck, Aluminium oxide GF_{254} (type 60/E, Al_2O_3) or Silica gel GF_{254} (type 60, SiO_2).

Photochemical Cycloaddition of 4-Methoxy-1-methylquinolin-2(1*H*)-one (2a) to Allene——Allene was bubbled into a solution of **2a** (255.8 mg) in 280 ml of methanol for 10 min and the whole was irradiated at ≥300 nm for 1 h. After removal of the solvent, the residue was chromatographed on silica gel (25 g). Elution with CH_2Cl_2–hexane–ether (5 : 5 : 1, v/v/v) afforded first the pure head-to-head adduct (**8a**), then a mixture of the two regioisomers, and finally the head-to-tail adduct (**7a**). The portion containing the mixture was separated further by PTLC [SiO_2 with CH_2Cl_2–ether (10 : 1, v/v) as a developing solvent]. Combined yields of **7a** and **8a** were 164.9 mg (53%) and 30.1 mg (10%), respectively.

8b-Methoxy-4-methyl-1-methylene-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one (**7a**), mp 80.5—82 °C (ether–hexane), UV λ_{max}^{MeOH} nm: 215, 256, 285 sh, 294 sh. IR (KBr): 1660 cm^{-1}. NMR ($CDCl_3$) δ: 2.1—3.2 (m, 2H), 3.04 (s, 3H), 3.34 (s, 3H), 3.44 (t, J=9 Hz, 1H), 4.82 (br s, 1H), 5.19 (br s, 1H), 6.7—7.5 (m, 4H). MS *m/z*: 229 (M^+), 189 (M−40). *Anal.* Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.45; H, 6.53; N, 6.06.

8b-Methoxy-4-methyl-2-methylene-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one (**8a**), oil, UV λ_{max}^{MeOH} nm: 215, 256, 285 sh, 294 sh. IR (film): 1665 cm^{-1}. NMR ($CDCl_3$) δ: 2.6—3.7 (m, 2H), 2.95 (s, 3H), 3.33 (s, 3H), 3.94 (br s, 1H), 4.85 (m, 1H), 5.05 (m, 1H), 6.8—7.5 (m, 4H). High resolution MS *m/z*: M^+ Calcd for $C_{14}H_{15}NO_2$: 229.1101. Found: 229.1084.

Photochemical Cycloaddition of 4-Methoxyquinolin-2(1*H*)-one (2b) to Allene——Compound **2b** (241.2 mg) was irradiated under the same conditions as above. The product obtained after evaporation of the solvent was recrystallized from acetone to give **7b**. The mother liquor afforded, after column chromatography (SiO_2, 15 g, 2% MeOH–CH_2Cl_2), a further amount of the same product. No other product was detected. The yield of **7b** was 228.9 mg (77%).

8b-Methoxy-1-methylene-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one (**7b**), mp 151.5—153.5 °C (ether), UV λ_{max}^{MeOH} nm: 218, 252, 263 sh, 287 sh, 297 sh, IR (KBr): 1685 cm^{-1}. NMR ($CDCl_3$) δ: 2.1—3.7 (m, 3H), 3.05 (s, 3H), 4.84 (br s, 1H), 5.24 (br s, 1H), 6.6—7.5 (m, 4H), 9.59 (br s, NH). High resolution MS *m/z*: M^+ Calcd for $C_{13}H_{13}NO_2$: 215.0944. Found: 215.0934.

Catalytic Hydrogenation of 8b-Methoxy-4-methyl-1-methylene-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one (7a)——The head-to-tail adduct (**7a**, 100.8 mg) was hydrogenated in methanol (8 ml) in the presence of 30 mg of 10% Pd/C at room temperature. After usual work-up, the residue was separated by PTLC (SiO_2, 5% MeOH–CH_2Cl_2) to give 60.6 mg (60%) of the *exo*-isomer (**9a**-*exo*: Rf=0.55) and 24.1 mg (24%) of the *endo*-isomer (**9a**-*endo*: Rf=0.40).

9a-*exo*, mp 66—67 °C (ether–hexane), IR (KBr): 1670 cm^{-1}. NMR ($CDCl_3$) δ: 1.27 (d, J=7.0 Hz, 3H), 1.78 (dd, J=9.4, 1.2 Hz, 1H), 1.88 (d, J=9.4 Hz, 1H), 2.2—2.8 (m, 1H), 2.85 (s, 3H), 3.34 (s, 3H), 3.39 (t, J=9.4 Hz, 1H), 6.7—7.4 (m, 4H). High resolution MS *m/z*: M^+ Calcd for $C_{14}H_{17}NO_2$: 231.1258. Found: 231.1259.

9a-*endo*, mp 124—128 °C (ether–hexane), IR (KBr): 1660 cm^{-1}. NMR ($CDCl_3$) δ: 0.86 (d, J=6.6 Hz, 3H), 1.7—3.0 (m, 3H), 2.87 (s, 3H), 3.20 (t, J=8.8 Hz, 1H), 3.32 (s, 3H), 6.6—7.4 (m, 4H). High resolution MS *m/z*: M^+ Calcd for $C_{14}H_{17}NO_2$: 231.1258. Found: 231.1259.

Synthesis of 1,4-Dimethyl-8b-methoxy-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one (9a) from 4-Methoxy-1-methyl-2-quinolone (2a) and Propene——Propene was bubbled through a solution of **2a** (180.7 mg) in methanol (280 ml) under irradiation at ≥300 nm for 2 h. After evaporation of the solvent, the residue was chromatographed on silica gel (10 g) as above to give 171 mg (78%) of **9a**-*exo* and 17 mg (8%) of **9a**-*endo*. These products were identical with the samples obtained by catalytic hydrogenation of **7a** on the basis of mixed melting point determinations and comparison of NMR and IR spectra.

1,4-Dimethyl-1,2-dihydrocyclobuta[*c*]quinolin-3(4*H*)-one (6a)——Compound **9a**-*exo* (102.1 mg) was dissolved in methanol (8 ml). After addition of two pellets of KOH (*ca.* 175 mg), the whole was refluxed for 2.5 h. After evaporation of the methanol and addition of 2 ml of water, the residue was extracted with 5% MeOH–CH_2Cl_2. The organic layer was washed with saturated aq. NaCl solution and then dried over Na_2SO_4. The residue obtained by evaporation of the solvent was passed through a short column of silica gel to give 83.6 mg (95%) of **6a**, mp 101.5—102.5 °C (hexane–ether). IR (KBr): 1670, 1588, 1450, 1280, 1220, 1195, 988, 963, 930, 765, 760, 725 cm^{-1}. NMR ($CDCl_3$) δ: 1.46 (d, J=7.0 Hz, 3H), 2.62 (dd, J=13.0, 1.6 Hz, 1H), 3.29 (dd, J=13.0, 4.2 Hz, 1H), 3.3—3.8 (m, 1H), 3.61 (s, 3H), 6.8—7.7 (m, 4H). High resolution MS *m/z*: M^+ Calcd for $C_{13}H_{13}NO$: 199.0996. Found: 199.0975. The product was identical (mixed melting point determination and comparison of IR spectra) with the sample obtained from 1-methyl-2-quinolone (**1a**) by Chiba *et al.*[12,13] by the route (**1a**→**4a**→**5a**→**6a**) shown in Chart 1.

2,4-Dimethyl-1,2-dihydrocyclobuta[*c*]quinolin-3(4*H*)-one (6a′)——The head-to-head adduct **8a** (19.6 mg) was hydrogenated as in the case of **7a** to **9a** to give quantitatively the two stereoisomers (**10a**-*endo* and **10a**-*exo*) in *ca.* 3 : 1 ratio. The NMR spectrum of the product showed the 2-methyl signal of the *endo*-isomer at δ 0.86 (d, J=6.4 Hz) and that of the *exo*-isomer at δ 1.26 (d, J=7.0 Hz), in an intensity ratio of approximately 3 : 1. Treatment of this mixture with KOH in methanol as above (**9a**-*exo*→6a) gave 15.5 mg (91%) of **6a′**, mp 98—99 °C (hexane–ether). IR (KBr): 1655, 1628, 1595, 1446, 1293, 1220, 1192, 957, 770, 744, 733 cm^{-1}. NMR ($CDCl_3$) δ: 1.44 (d, J=6.8 Hz), 2.63 (dd, J=13.6, 1.2 Hz, 1H), 3.1—3.8 (m, 2H), 3.62 (s, 3H), 6.8—7.6 (m, 4H). High resolution MS *m/z*: M^+ Calcd for $C_{13}H_{13}NO$: 199.0996. Found: 199.0976. Nonidentity of this compound with **6a** was confirmed by mixed melting point

determination (mp 65—82 °C) and comparison of IR spectra.

Photocycloaddition of 4-Methoxy-1-methyl-2-quinolone (2a) to Diketene——A solution of **2a** (300.4 mg) in methanol (280 ml) containing 4.058 g (30 mol eq) of diketene was irradiated for 1 h under a current of argon. After evaporation of the solvent, the residue was chromatographed over silica gel (40 g). Elution with CH_2Cl_2–hexane–ether (7:3:1, v/v/v) gave the *endo*-adduct and elution with CH_2Cl_2–ether (10:1, v/v) gave the *exo*-adduct. The portion containing both isomers (obtained between the above two fractions) was further separated by the same procedure. The yields of **11a**-*endo* and **11a**-*exo* were 160.9 mg (37%) and 221.4 mg (51%), respectively.

endo-Isomer of 8b-methoxy-4-methyl-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one-1-spiro-2′-(oxetan)-4′-one (**11a**-*endo*), mp 163—164.5 °C (benzene–hexane). IR (KBr): 1830, 1665 cm^{-1}. NMR ($CDCl_3$) δ: 2.15 (dd, J= 11.2, 10.2 Hz, 1H), 2.60 (dd, J=11.2, 8.8 Hz, 1H), 2.95 (dd, J=10.2, 8.8 Hz, 1H), 2.93 (s, 3H), 3.37 (s, 3H), 3.21 and 4.15 (each d, J=15.8 Hz, each 1H), 6.85—7.5 (m, 4H). MS m/z: 273 (M^+), 189. *Anal.* Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 66.03; H, 5.66; N, 5.06.

exo-Isomer (**11a**-*exo*), mp 138—140 °C (ether). IR (KBr): 1832, 1658 cm^{-1}. NMR ($CDCl_3$) δ: 2.30 (dd, J=12.6, 7.5 Hz, 1H), 2.98 (dd, J=12.6, 10.5 Hz), 2.95 and 3.35 (each d, J=16.3 Hz, each 1H), 3.05 (s, 3H), 3.36 (s, 3H), 3.58 (dd, J=10.5, 7.5 Hz, 1H), 6.9—7.6 (m, 4H). MS m/z: 273 (M^+), 189. *Anal.* Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.98; H, 5.71; N, 4.89.

Pyrolytic Elimination of Carbon Dioxide from the Adducts (11a) Obtained by Photoaddition of 4-Methoxy-1-methyl-2-quinolone (2a) to Diketene——The adduct **11a**-*exo* (140.5 mg) was heated for 30 min in an oil bath (200—210 °C). The product was separated by PTLC (SiO_2, 2% MeOH containing CH_2Cl_2–AcOEt, 5:1, v/v) to give 100.1 mg (85%) of the 1-methylene derivative (**7a**). This reaction can also be carried out in a sealed tube. The 1-methylene derivative was identical with the major adduct (**7a**) obtained by photoaddition of 4-methoxy-1-methyl-2-quinolone (**2a**) to allene.

Photoaddition of 1,4-Dimethyl-2-quinolone (3) to Allene——Allene was bubbled through a solution of **3** (266.5 mg) in methanol (200 ml) under irradiation at ≥300 nm for 1 h. The residue (389 mg) obtained after removal of the solvent was chromatographed over silica gel (16 g). Elution with 1% ether–CH_2Cl_2 afforded 250.2 mg (76.2%) of the [2+2] adduct (**13**) as the sole isolable product, mp 41—42 °C (hexane–ether). UV λ_{max}^{MeOH} nm: 215, 258, 269 sh, 283 sh, 290 sh. IR (KBr): 1650 cm^{-1}. NMR ($CDCl_3$) δ: 1.49 (s, 3H), 2.85—3.2 (m, 3H), 3.34 (s, 3H), 4.65—4.75 (m, 1H), 4.88—5.05 (m, 1H), 6.75—7.35 (m, 4H). High resolution MS m/z: M^+ Calcd for $C_{14}H_{15}NO$: 213.1153. Found: 213.1173.

This compound was identical (mixed melting point determination and comparison of IR and NMR spectra) with the sample prepared from **3** and diketene according to the procedure (**3**→**12**→**13**) described by Chiba *et al.*[12]

Photoaddition of 1,4-Dimethyl-2-quinolone (3) to Diketene——A sqlution of **3** (203.4 mg) in acetonitrile (165 ml) containing 5.333 g (55 mol eq) of diketene was irradiated at ≥300 nm for 1 h under a current of argon. The reaction mixture was concentrated under reduced pressure. The residue was chromatographed on silica gel (25 g). Elution with 2% ether–CH_2Cl_2 afforded the *exo*-adduct, followed by a mixture of the *endo*- and *exo*-isomers, and then by pure *endo*-adduct. The portion containing both isomers was subjected to PTLC (SiO_2, CH_2Cl_2–ether, 5:1, v/v) to give further amounts of the *exo*- (Rf=0.68) and *endo*-isomers (Rf=0.51). Total yields of **12**-*exo*- and **12**-*endo*-isomers were 176.1 mg (58%) and 97.6 mg (32%), respectively.

12-*exo*, mp 131—132 °C (benzene–hexane). UV λ_{max}^{MeOH} nm: 211, 256, 280 sh, 290 sh. IR (KBr): 1836, 1652 cm^{-1} NMR ($CDCl_3$) δ: 1.69 (s, 3H), 2.82 (dd, J=20.0, 9.4 Hz, 1H), 2.84 (dd, J=20.0, 9.4 Hz, 1H), 2.98 and 3.12 (each d, J=16.0 Hz, each 1H), 3.30 (t, J=9.4 Hz, 1H), 3.33 (s, 3H), 6.8—7.45 (m, 4H). MS m/z: 257 (M^+), 173. *Anal.* Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.09; H, 5.87; N, 5.37. This compound was identical with the major adduct obtained from the photoaddition reaction of **3** with diketene under similar conditions.[12]

12-*endo*, mp 176—177.5 °C (dec.) (benzene). UV λ_{max}^{MeOH} nm: 212, 256, 267 sh, 282 sh, 291 sh. IR (KBr): 1820, 1655 cm^{-1}. NMR ($CDCl_3$) δ: 1.48 (s, 3H), 2.6—2.8 (m, 3H), 3.24 and 3.73 (each d, J=16.0 Hz, each 1H), 3:34 (s, 3H), 6.8—7.4 (m, 4H). MS m/z: 257 (M^+), 173. *Anal.* Calcd for $C_{15}H_{15}NO_3$: C, 70.02; H, 5.88; N, 5.44. Found: C, 70.29; H, 5.81; N, 5.41. This compound was identical with the minor adduct obtained from the photoaddition reaction of **3** with diketene under similar conditions.[12]

Oxidation of the Allene Adduct (13) to 4,8b-Dimethyl-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinoline-1,3(4*H*)-dione (14)——A solution of *ca.* 1 mg of osmium tetroxide in a small amount of benzene was added to a solution of **13** (13.5 mg) in a mixture of dioxane–water (3:2, v/v, 5 ml). Under stirring, 27 mg (2 mol eq) of $NaIO_4$ was added portionwise to the above mixture and the whole was stirred at room temperature for 2.5 h. After addition of water, the product was taken up in dichloromethane. This solution was washed with water and dried over Na_2SO_4, then the solvent was removed. The residue obtained was separated by PTLC (SiO_2, 5% MeOH–CH_2Cl_2) to give 7.7 mg (56.5%) of the 1-oxo derivative (**14**: Rf=0.5), mp 101—102 °C (hexane–ether). UV λ_{max}^{MeOH} nm: 217, 259. IR (KBr): 1778, 1660 cm^{-1}. NMR ($CDCl_3$) δ: 1.54 (s, 3H), 2.95—3.55 (m, 3H), 3.39 (s, 3H), 6.8—7.4 (m, 4H). High resolution MS m/z: M^+ Calcd for $C_{13}H_{13}NO_2$: 215.0946. Found: 215.0950.

Preparation of 1,2,2a,8b-Tetrahydrocyclobuta[*c*]quinoline-1,3(4*H*)-dione (14) from 1,4-Dimethyl-2-quinolone (3) and Diethyl Ketene Acetal——A solution of **3** (285.8 mg) in acetonitrile (180 ml) containing 0.5 ml of triethylamine and an excess of diethyl ketene acetal[15] (*tert*-BuOH solution) was irradiated at ≥300 nm for 1 h. The residue

obtained after evaporation of the solvent was chromatographed over silica gel (15 g). Elution with 0.5% MeOH–CH_2Cl_2 afforded 173.0 mg (36%) of 1,1-diethoxy-4,8b-dimethyl-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one (**17**). Oil. UV λ_{max}^{MeOH} nm: 215, 259. IR (film): 1660 cm^{-1}. NMR ($CDCl_3$) δ: 0.87 (t, J=6.8 Hz, 3H), 1.18 (t, J=6.8 Hz, 3H), 1.56 (s, 3H), 2.4—2.95 (m, 3H), 2.95—3.7 (m, 4H), 3.32 (s, 3H), 6.7—7.35 (m, 4H). MS *m/z*: 289 (M^+), 261, 244.

The adduct (**17**: 40.6 mg) was dissolved in a mixture of dioxane–water (3:2, v/v) containing two drops of conc. HCl at 0 °C. The mixture was then stirred at room temperature for 4 h. After addition of water, the product was extracted with dichloromethane, and the extract was washed with water and dried over Na_2SO_4. The residue after evaporation of the solvent was separated by PTLC (SiO_2, 9% MeOH–CH_2Cl_2) to give 24.6 mg (81%) of the 1-oxo derivative (**14**: Rf=0.9.). The compound was identical with the sample obtained by osmium tetroxide oxidation of the allene adduct (**13**).

Baeyer–Villiger Oxidation of 4,8b-Dimethyl-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-1,3(4*H*)-one (14) to the γ-Lactone (15)——*m*-Chloroperbenzoic acid (MCPBA, 50 mg) was added to a solution of the ketone (**14**: 14.8 mg) in chloroform (2 ml), and the whole was refluxed for 2 h, then cooled. After addition of CH_2Cl_2, the whole was washed with 10% aq. $NaHCO_3$ and then with water and dried over Na_2SO_4. The residue obtained after removal of the solvent was separated by PTLC (SiO_2, 7% MeOH–CH_2Cl_2) to give 10.2 mg (64%) of the γ-lactone (**15**: Rf=0.8) as an oil. UV λ_{max}^{MeOH} nm: 209, 254, 280 sh, 290 sh. IR (film): 1780, 1670 cm^{-1}. NMR ($CDCl_3$) δ: 1.70 (s, 3H), 2.48 (dd, J=12, 16 Hz, 1H), 2.94 (dd, J=8, 16H, 1H), 3.36 (s, 3H), 3.37 (dd, J=8, 12 Hz, 1H), 6.7—7.55 (m, 4H). MS *m/z*: 231 (M^+).

1,4-Dimethyl-3-methoxycarbonylmethylquinolin-2(1*H*)-one (16)——Boron trifluoride etherate (0.1 ml, 47% solution) was added to a solution of the γ-lactone (**15**: 10.2 mg) in benzene (1 ml), and the whole was stirred for 45 min at room temperature. The crystalline material participated in the reaction mixture. Methanol (2 ml) was added to the residue obtained after rapid evaporation of the benzene and the mixture was stirred overnight. The residue obtained after evaporation of the solvent was separated by PTLC (SiO_2, 5% MeOH–CH_2Cl_2) to give 10.5 mg (97%) of the methyl ester (**16**, Rf=0.6), mp 99.5—100 °C. UV λ_{max}^{MeOH} nm: 228, 272, 282 sh, 327, 343 sh. IR (KBr): 1725, 1638 cm^{-1}. NMR ($CDCl_3$) δ: 2.42 (s, 3H), 3.65 and 3.68 (s, each 3H), 3.79 (s, 2H), 6.95—7.55 (m, 3H), 7.65 (br d, J=7 Hz, 1H). High resolution MS *m/z*: M^+ Calcd for $C_{14}H_{15}NO_3$: 245.1051. Found: 245.1042.

Photoaddition of 4-Methoxy-6-methyl-2-pyridone (18a) to Allene——Allene was bubbled through a solution of the pyridone (**18a**, 214.7 mg) in acetone (270 ml) under irradiation at ≥300 nm for 2.5 h. The residue obtained after evaporation of the solvent was chromatographed over silica gel (30 g). Elution with 2% MeOH–CH_2Cl_2 afforded first 95.9 mg (42% based on the consumed pyridone) of the head-to-tail adduct (**20a**) and then 35.8 mg of the starting pyridone.

20a, mp 171—173 °C (ether). UV λ_{max}^{MeOH} nm: 258. IR (KBr): 1687, 1664 cm^{-1}. NMR ($CDCl_3$) δ: 1.91 (d, J=1.1 Hz, 1H), 2.3—3.5 (m, 3H), 3.16 (s, 3H), 4.55 (br s, 1H), 4.80 (br s, 1H), 4.99 (br s, 1H), 7.88 (br s, 1H). MS *m/z*: 179 (M^+). *Anal.* Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 66.74; H, 7.34; N, 7.69.

5-Methyl-1-methylene-1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one (21)——The adduct **20a** (19.8 mg) was dissolved in methanol (3 ml). After addition of KOH (*ca.* 80 mg), the solution was refluxed for 2 h. The residue obtained after evaporation of the solvent was dissolved in 5% MeOH–CH_2Cl_2. After being washed with sat. aq. NaCl, the organic layer was dried over Na_2SO_4. The product thus obtained was purified by PTLC (SiO_2, 5% MeOH–CH_2Cl_2) to give 16.2 mg (99%) of **21**, mp 205—206.5 °C (acetone–hexane). UV λ_{max}^{MeOH} nm: 227.5, 234, 250 sh, 315. IR (KBr): 1685, 1665, 1643 cm^{-1}. NMR ($CDCl_3$) δ: 2.34 (s, 3H), 3.45 (s, 2H), 4.97 (s, 1H), 5.25 (s, 1H), 5.94 (s, 1H), 12.45 (br s, NH). *Anal.* Calcd for C_9H_9NO: C, 73.45; H, 6.16; N, 9.52. Found: C, 73.30; H, 6.25; N, 9.23.

Synthesis of 5-Methyl-1-methylene-1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one (21) from 4-Acetoxy-6-methyl-2-pyridone (18b)——Allene was bubbled through a solution of **18b** (303 mg) in acetone (290 ml) under irradiation at ≥300 nm for 6 h. The residue after evaporation of the solvent was chromatographed over silica gel (30 g). Elution with 1% MeOH–CH_2Cl_2 afforded 27.6 mg of **21** and then a fraction containing the adduct with some impurity (130 mg). This fraction was dissolved in methanol (2 ml) and after addition of KOH (*ca.* 100 mg), the whole was stirred at room temperature for 2 h. The product thus obtained was separated by PTLC (SiO_2, 5% MeOH–CH_2Cl_2) to give 23.9 mg of **21**. The total yield of **21** was 51.5 mg (19%). The product was identical with the sample obtained from **18a** *via* **20a**.

1,5-Dimethyl-1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one (22)——(a) Catalytic hydrogenation of **21**. A solution of **21** (20.1 mg) in methanol (4 ml) was hydrogenated over 10% Pd/C (6 mg) at room temperature for 5 min. After removal of the catalyst by filtration, the filtrate was concentrated. The residue was separated by PTLC (SiO_2, 5% MeOH–CH_2Cl_2) to give 16.3 mg (88%) of **22**, mp 144—145 °C (ether). UV λ_{max}^{MeOH} nm: 233, 296. IR (KBr): 1662, 1611 cm^{-1}. NMR ($CDCl_3$) δ: 1.31 (d, J=6.8 Hz, 3H), 2.32 (s, 3H), 2.2—2.8 (m, 1H), 3.0—3.5 (m, 2H). 5.85 (s, 1H), 12.65 (br s, NH). MS *m/z*: 149 (M^+).

(b) *Via* photoaddition of **18b** to propene. A solution of **18b** (214 mg) in acetone (280 ml) was irradiated at ≥300 nm for 5 h. The residue obtained after evaporation of the solvent was chromatographed over silica gel (30 g). Elution with 1% MeOH–CH_2Cl_2 gave first 166.6 mg (62%) of the adduct (**23b**) and then 10.0 mg (5%) of **22**.

23b, mp 154.5—156 °C (acetone–hexane). UV λ_{max}^{MeOH} nm: 250. IR (KBr): 1738, 1692, 1668 cm^{-1}. NMR ($CDCl_3$) δ: 1.16 (d, J=7.2 Hz, 3H), 1.86 (d, J=1.2 Hz, 3H), 1.96 (s, 3H), 1.6—2.7 (m, 3H), 3.28 (t, J=9.6 Hz, 1H), 4.78 (s, 1H), 8.58 (br s, NH). MS *m/z*: 209 (M^+), 167.

The adduct (**23b**, 41.1 mg) was dissolved in methanol (4 ml) containing KOH (*ca.* 80 mg) and the whole was stirred at room temperature for 1.5 h. After evaporation and addition of water, the product was extracted with 5% MeOH–CH_2Cl_2. The organic layer was washed with sat. aq. NaCl and dried over Na_2SO_4. The residue obtained after evaporation of the solvent was purified by PTLC (SiO_2, 5% MeOH–CH_2Cl_2) to give 28.4 mg (97%) of **22**, which was identical with the sample obtained in (a).

Photoaddition of 4-Methoxy-1-methyl-2-pyridone (19a) to Allene——Allene was bubbled into a solution of **19a** (201.9 mg) in acetone (270 ml) for *ca.* 10 min, then the whole was irradiated at ≥300 nm for 50 min. The residue obtained after evaporation of the solvent was chromatographed over silica gel (18 g). Elution with 1% MeOH/CH_2Cl_2–AcOEt (19 : 1, v/v) gave 54.8 mg (29% based on the consumed **19a**) of the head-to-tail adduct (**25a**). Elution with 5% MeOH/CH_2Cl_2–AcOEt (19 : 1, v/v) afforded 58.1 mg of the starting pyridone (**19a**).

6a-Methoxy-4-methyl-1-methylene-1,2,2a,6a-tetrahydrocyclobuta[*c*]pyridin-3(4*H*)-one (**25a**), oil. UV λ_{max}^{MeOH} nm: 257. IR (film): 1655 cm^{-1}. NMR ($CDCl_3$) δ 2.3—2.9 (m, 2H), 3.05 (s, 3H), 3.16 (s, 3H), 3.27 (td, J=9.0, 1.8 Hz, 1H), 4.79 (dd, J=8.0, 1.8 Hz, 1H), 4.7—5.1 (m, 2H), 6.15 (d, J=8.0 Hz, 1H). High resolution MS *m/z*: M^+ Calcd for $C_{10}H_{13}NO_2$: 179.0943. Found: 179.0945.

Photoaddition of 4-Methoxy-1-methyl-2-pyridone (19a) to Diketene——A solution of **19a** (152.8 mg) in acetone (200 ml) containing diketene (3.45 g, 37 mol eq) was irradiated at ≥300 nm for 2 h under an argon atmosphere. The residue obtained after evaporation of the solvent was separated by column chromatography (SiO_2, 25 g). Elution with 1% MeOH–CH_2Cl_2 containing 3% (v/v) AcOEt afforded a mixture of two adducts, which was separated further by PTLC (SiO_2, 5% MeOH–CH_2Cl_2–AcOEt, 9 : 1, v/v) to give 24.1 mg (20%) of one adduct (designated as **24a**-A, Rf=0.5) and then 23.8 mg (20%) of the other adduct (**24a**-B, Rf=0.38).

24a-A, mp 132—133.5 °C (benzene–hexane). UV λ_{max}^{MeOH} nm (log ε): 258 (3.70). IR (KBr): 1833, 1665, 1655 cm^{-1}. NMR ($CDCl_3$) δ: 2.1—3.2 (m, 2H), 2.68 (td, J=6.8, 1.4 Hz, 1H), 3.10 (s, 3H), 3.13 (s, 3H), 3.14 and 3.95 (each d, J=16.4 Hz, each 1H), 4.91 (dd, J=8.0, 1.4 Hz, 1H), 6.42 (d, J=8.0 Hz, 1H). MS *m/z*: 223 (M^+), 139. *Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.29; H, 5.98; N, 6.08.

24a-B, mp 131.5—134 °C (dec.) (benzene–hexane). UV λ_{max}^{MeOH} nm: 258. IR (KBr): 1835, 1825, 1670, 1655 cm^{-1}. NMR ($CDCl_3$) δ: 2.20 (dd, J=12.9, 9.6 Hz, 1H), 2.70 (dd, J=12.9, 9.6 Hz, 1H), 3.11 (s, 3H), 3.16 (s, 3H), 3.08 and 3.49 (each d, J=17.0 Hz, each 1H), 3.43 (td, J=9.6, 2.1 Hz, 1H), 4.78 (dd, J=8.2, 2.1 Hz, 1H), 6.41 (d, J=8.2 Hz, 1H). MS *m/z*: 223 (M^+), 139. *Anal.* Calcd for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 58.98; H, 5.81; N, 6.12.

6a-Methoxy-4-methyl-1-methylene-1,2,2a,6a-tetrahydrocyclobuta[*c*]pyridin-3(4*H*)-one (25a)——The adduct **24a**-A (95.5 mg) was heated on an oil bath (bath temperature was *ca.* 200 °C) for 20 min. The product was purified by PTLC (SiO_2, 5% MeOH/CH_2Cl_2–AcOEt, 9 : 1, v/v) to give 56.8 mg (74%) of the product. No other product was detected. Compound **24a**-B also gave the same product under the same conditions. The product was identified with **25a** formed by photoaddition of **19a** to allene by mixed melting point determination and comparison of spectral data.

4-Methyl-1-methylene-1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one (26a)——A solution of 6a-methoxy-4-methyl-

Table II. Crystal Data for **4a**-*exo*

Molecular formula	$C_{14}H_{13}NO_3$
Molecular weight	243.2621
Crystal system	Orthorhombic
Lattice constants	a 10.2247(5) Å
	b 23.4064(20) Å
	c 10.1153(7) Å
	$\alpha=\beta=\gamma=90°$
	V 2420.83 Å^3
Systematic absences	0k1 : l odd
	h01 : h odd
	hk0 : k odd
	(h00 : h odd)
	(0k0 : k odd)
	(001 : l odd)
Space group	*Pcab*
Number of molecules in a unit cell	Z=8
Calculated density	1.325 g/cm^3
Observed density	1.321 g/cm^3
Radiation used	Cu K_α
Theta range	$3° < \theta < 78°$
No. of obsd. reflections	1586

TABLE III. Positional Parameters ($\times 10^4$) and Thermal Parameters of **4a**-*exo* with Their Estimated Standard Deviations in Parentheses

	X	Y	Z	B_{iso}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	8495 (4)	1798 (1)	1754 (3)	2.74 (0.09)	0.0076 (4)	0.0013 (1)	0.0055 (3)	0.0003 (1)	0.0003 (3)	−0.0001 (1)
C(2)	9189 (4)	2375 (2)	1642 (4)	3.93 (0.11)	0.0109 (5)	0.0012 (1)	0.0113 (5)	0.0001 (2)	0.0007 (4)	0.0003 (2)
C(2a)	10482 (4)	2051 (2)	1938 (4)	3.40 (0.10)	0.0096 (5)	0.0013 (1)	0.0081 (4)	−0.0007 (2)	−0.0001 (4)	−0.0002 (1)
C(3)	11183 (4)	1884 (2)	677 (4)	3.66 (0.11)	0.0075 (4)	0.0019 (1)	0.0092 (4)	−0.0006 (2)	−0.0001 (4)	0.0003 (2)
N(4)	11369 (4)	1316 (1)	420 (3)	3.90 (0.09)	0.0100 (4)	0.0018 (1)	0.0087 (4)	0.0003 (1)	0.0032 (3)	0.0005 (1)
C(5)	11433 (5)	308 (2)	1083 (5)	4.92 (0.14)	0.0119 (6)	0.0020 (1)	0.0130 (6)	0.0018 (2)	0.0037 (5)	−0.0001 (2)
C(6)	11041 (5)	−131 (2)	1911 (5)	5.35 (0.15)	0.0160 (7)	0.0014 (1)	0.0152 (7)	0.0015 (2)	0.0020 (6)	0.0004 (2)
C(7)	10184 (5)	−25 (2)	2929 (5)	4.75 (0.13)	0.0140 (6)	0.0015 (1)	0.0126 (6)	0.0002 (2)	0.0003 (5)	0.0009 (2)
C(8)	9747 (4)	524 (2)	3137 (4)	3.59 (0.11)	0.0099 (5)	0.0015 (1)	0.0080 (4)	0.0001 (2)	0.0007 (4)	0.0006 (2)
C(8b)	9657 (4)	1562 (1)	2549 (4)	2.76 (0.09)	0.0080 (4)	0.0013 (1)	0.0052 (3)	−0.0000 (1)	−0.0002 (3)	−0.0002 (1)
C(4a)	10978 (4)	860 (2)	1279 (4)	3.32 (0.10)	0.0076 (4)	0.0016 (1)	0.0081 (4)	0.0005 (2)	0.0007 (4)	0.0003 (2)
C(8́a)	10126 (3)	967 (1)	2328 (4)	2.73 (0.09)	0.0065 (4)	0.0013 (1)	0.0066 (4)	0.0001 (1)	−0.0010 (3)	0.0002 (1)
O(C3)	11571 (3)	2256 (1)	−79 (3)	4.96 (0.09)	0.0143 (4)	0.0021 (1)	0.0105 (4)	−0.0017 (1)	0.0019 (3)	0.0012 (1)
C(9)	12102 (6)	1168 (2)	−788 (6)	7.17 (0.20)	0.0226 (10)	0.0029 (1)	0.0140 (7)	0.0016 (3)	0.0122 (7)	0.0011 (3)
O(1′)	7181 (2)	1775 (1)	2351 (2)	3.03 (0.06)	0.0079 (3)	0.0015 (0)	0.0059 (3)	0.0004 (1)	0.0006 (2)	0.0001 (1)
C(3′)	7969 (4)	1485 (2)	525 (4)	3.49 (0.10)	0.0101 (5)	0.0018 (1)	0.0056 (4)	0.0007 (2)	−0.0008 (4)	−0.0005 (2)
C(4′)	6677 (4)	1504 (2)	1248 (4)	3.48 (0.10)	0.0109 (5)	0.0011 (1)	0.0082 (4)	0.0004 (2)	−0.0009 (4)	0.0006 (1)
O(C4′)	5578 (3)	1362 (1)	1080 (3)	4.68 (0.09)	0.0097 (3)	0.0018 (1)	0.0147 (4)	−0.0006 (1)	−0.0025 (3)	0.0005 (1)
H(C2)	8946 (41)	2626 (18)	2437 (43)	5.86 (1.10)						
H′(C2)	9134 (45)	2550 (20)	688 (42)	6.36 (1.18)						
H(C2a)	11143 (41)	2265 (17)	2668 (42)	5.38 (1.07)						
H(C5)	12029 (40)	243 (16)	443 (42)	5.33 (1.11)						
H(C6)	11387 (45)	−559 (18)	1729 (44)	6.29 (1.20)						
H(C7)	9934 (45)	−334 (18)	3491 (45)	6.10 (1.20)						
H(C8)	9150 (34)	629 (14)	3833 (34)	2.91 (0.80)						
H(C8b)	9574 (36)	1626 (15)	3448 (37)	3.85 (0.89)						
H(C3′)	8321 (41)	1035 (17)	342 (42)	5.33 (1.10)						
H′(C3′)	8038 (46)	1728 (20)	−472 (49)	7.70 (1.41)						
H(C9)	12114 (50)	1421 (20)	−1229 (51)	7.90 (1.44)						
H′(C9)	11580 (57)	788 (24)	−1346 (58)	11.12 (1.83)						
H″(C9)	13070 (62)	977 (26)	−625 (65)	12.82 (2.16)						

1-methylene-1,2,2a,6a-tetrahydrocyclobuta[*c*]pyridine-3(4*H*)-one (**25a**: 43.6 mg) in methanol (4 ml) containing KOH (*ca.* 85 mg) was refluxed for 3 h. After evaporation and addition of water, the whole was extracted with CH_2Cl_2. The residue obtained was purified by PTLC (SiO_2, 7% MeOH–CH_2Cl_2) to give 22.9 mg (60%) of **26a**, mp 87—88.5 °C. UV λ_{max}^{MeOH} nm: 228, 235, 313. IR (KBr): 1673, 1643, 1580, 1547 cm^{-1}. NMR ($CDCl_3$) δ: 3.46 (br s, 2H), 3.51 (s, 3H), 4.99 (br s, 1H), 5.26 (br s, 1H), 6.07 (d, J=6.5 Hz, 1H), 7.21 (d, J=6.5 Hz, 1H). High resolution MS *m/z*: M^+ Calcd for C_9H_9NO: 147.0683. Found: 147.0682.

6a-Methoxy-1-methylene-1,2,2a,6a-tetrahydrocyclobuta[*c*]pyridin-3(4*H*)-one (25b)——Allene was bubbled through a solution of 4-methoxy-2-pyridone (**19b**; 201 mg) in acetone (280 ml) under irradiation at ≥300 nm for 3 h. The residue obtained after evaporation of the solvent was separated by column chromatography (SiO_2, 25 g). Elution with ether–hexane (3 : 1, v/v) gave 14.6 mg of unidentified product (the structure is now under investigation) and then 103.6 mg (55% based on the consumed **19b**) of the head-to-tail adduct (**25b**). Elution with 5% MeOH–CH_2Cl_2 gave 57.5 mg of the starting material (**19b**).

25b, mp 127—128 °C (ether). UV λ_{max}^{MeOH} nm: 257. IR (KBr): 1679, 1646 cm^{-1}. NMR ($CDCl_3$) δ: 2.5—3.4 (m, 3H), 3.17 (s, 3H), 4.79 (d, J=8.0 Hz, 1H), 4.84 (s, 1H), 5.02 (s, 1H), 6.19 (dd, J=8.0, 5.2 Hz, 1H), 7.89 (br s, NH). MS *m/z*: 165 (M^+). *Anal.* Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.39; H, 6.74; N, 8.41.

1-Methylene-1,2-dihydrocyclobuta[*c*]pyridin-3(4*H*)-one (26b)——A solution of the adduct **25b** (15.4 mg) obtained above in methanol (3 ml) containing KOH (*ca.* 80 mg) was refluxed for 1.5 h. After evaporation and addition of water, the whole was extracted with 5% MeOH–AcOEt. The organic layer was washed with sat. aq. NaCl and dried over Na_2SO_4. The residue obtained after evaporation was purified by PTLC (SiO_2, 5% MeOH–CH_2Cl_2) to give 12.2 mg (98%) of **26b**, mp 171—173 °C (acetone–hexane). UV λ_{max}^{MeOH} nm: 226, 233, 250 sh, 313. IR (KBr): 1678, 1645 cm^{-1}. NMR ($CDCl_3$) δ: 3.50 (s, 2H), 5.02 (s, 1H), 5.31 (s, 1H), 6.17 (d, J=6.4 Hz, 1H), 7.28 (d, J=6.4 Hz, 1H), 12.5 (br s, NH). MS *m/z*: 133 (M^+).

X-Ray Analysis of *exo*-Isomer of 4-Methyl-1,2,2a,8b-tetrahydrocyclobuta[*c*]quinolin-3(4*H*)-one-1-spiro-2′-(oxetan)-4′-one (4a-*exo*)——The crystals were grown in acetone solution as colorless prisms.[16] A computer-controlled Philips PW 1100 four-circle X-ray auto diffractometer was used for all measurements. The unit cell dimensions and orientation matrix were derived from a least-squares fit of the angular values of 20 reflections. The crystal data for **4a**-*exo* are given in Table II.

The intensities of all the reflections in the appropriate 2θ range were measured using a variable speed θ-2θ scan technique. The scan speed was 4 °/min for all reflections. The total number of reflections is given in Table II.

The structure of **4a**-*exo* was solved by the direct method using MULTAN[17] and refined by the block-diagonal least-squares procedure. A difference Fourier synthesis was used to locate the hydrogen atoms in **4a**-*exo*. The value of R was reduced to 6.17% after several cycles of least-squares calculation assuming anisotropic thermal parameters for the non-hydrogen atoms and isotropic ones for the hydrogen atoms. The final positional and thermal parameters are given in Table III. The atomic scattering factors for carbon and oxygen were taken from the International Tables for X-Ray Crystallography,[18] and those for hydrogen, from Stewart *et al.*[19]

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