Carboxypeptidase A Digestion of RNase Ms——Six mg of RNase Ms was dissolved in 6 ml of Tris–HCl buffer (0.1 M, pH 8.0) and to the reaction mixture 30 μl (0.8 mg) of carboxypeptidase A was added. The reaction mixture was shaken at 37° and the amino acids released in 0.3 ml aliquots were analyzed by an amino acid analyzer. Serine released was distinguished from glutamine and aspargine by its location on the chart of amino acid analysis and the ratio of color values at 570 nm and 440 nm. The ratios for serine, glutamine and aspargine were 5.8, 5.1 and 5.1, respectively in our amino acid analysis system.

CD Spectrum——Circular dichroism spectra of RNase Ms and carboxypeptidase treated RNase Ms were measured with a JASCO J-40 spectropolarimeter at room temperature. The cells having 0.5, 0.1 and 0.05 cm light path were used. The protein concentrations used for CD spectra measurement were 80—40 μM for 250—350 nm wavelength region and 20 μM for 200—250 nm region.

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Photochemical Synthesis of 5,10,11,12,12a,12b-Hexahydro-12b-hydroxyisoindolo[2,1-*a*]benz[*cd*]indol-5-one[1,2]

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Photocyclization of N-(5,6,7,8-tetrahydro-1-naphthyl)phthalimide (3) afforded 5,10,11,12,12a,12b-hexahydro-12b-hydroxyisoindolo[2,1-*a*]benz[*cd*]indol-5-one (4) in good yield. On acid treatment, 4 was readily dehydrated to give 5,10,11,12-tetrahydroisoindolo [2,1-*a*]benz[*cd*]indol-5-one (5).

Keywords——photochemical synthesis of heterocycles; Norrish type II reaction; benz[*cd*]indole system; photocyclization of N-substituted phthalimide; N-(5,6,7,8-tetrahydro-1-naphthyl)phthalimide

The photochemistry of aromatic cyclic imides, *e. g.*, phthalimides, has received intensive study[4] since its discovery in 1972,[5] and the most frequently reported transformations have been photocyclizations which are likely the Norrish type II reactions of the excited imide carbonyl group.[4,6] Earlier it was observed that N-*o*-tolylphthalimide (1) on irradiation undergoes cyclization to form a tetracyclic system (2) furnishing synthetically useful yield of cyclic pentanols[4] as shown in Chart. In a subsequent work[7] we examined the substituent effects either in the A or B ring of 1 on the photoreaction and, in a previous paper,[1] we described the results of a synthetic investigation with N-pyridylphthalimides as a variation

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3) Location: *a) Ishikari-Tobetsu, Hokkaido 061-02, Japan*; *b) Kita-12, Nishi-6, Kita-ku, Sapporo 060, Japan.*
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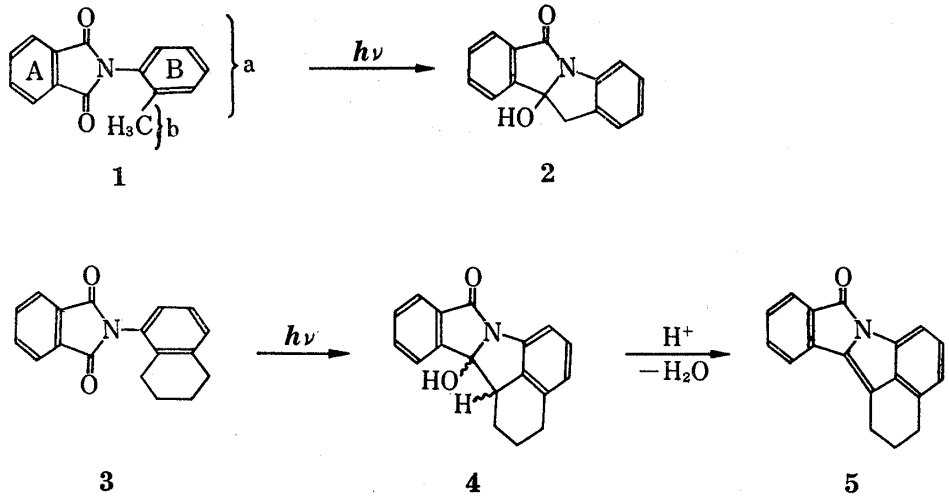
of the substitution in the B ring (a in **1**). In the present report we wish to note the photochemical reaction of N-(5,6,7,8-tetrahydro-1-naphthyl)phthalimide (**3**) as an example of a next logical structural variation for the substrate in which the methyl group of **1** is replaced by an alicyclic methylene moiety (b in **1**).



1 **2** **3** **4** **5**

Chart

An acetone solution of **3**, prepared by the thermal condensation of 5,6,7,8-tetrahydro-1-naphthylamine and phthalic anhydride, was irradiated with a 500 W high-pressure mercury lamp at room temperature for 25 min under a nitrogen atmosphere. The expected cyclized product (**4**) was obtained in a good isolated yield (77%). The structure of the pentacyclic system **4** was established by the elemental analysis and the spectral data [IR, 3300 cm^{-1} (OH), 1677 cm^{-1} (lactam C=O); NMR, δ 3.06 (Ar-C<u>H</u>: a methine proton formed by the cyclization), δ 9.00(O<u>H</u>)]. Dehydration of the resulting pentacyclic compound (**4**) to **5** was easily accomplished by refluxing **4** in a conc.HCl–ethanol (1: 10, v/v) mixture for 0.5 hr in 87% yield. Disapperance of methine and hydroxy protons in the nuclear magnetic resonance (NMR) spectrum and the absence of OH absorption in the infrared (IR) spectrum of **5** were all in accord with the assigned structure. Thus the photocyclization of **3** offers a simple and efficient synthetic route to the novel pentacyclic nitrogen-containing system (**4** and **5**).

In view of rich photoreactions exhibited by the imide carbonyl (**1**) as evidenced by the variation of the B ring (a in **1**) and the methyl (b in **1**) of the substrates, it is expected that a variety of multicyclic system containing a nitrogen will be synthetically accessible by the method. Studies of further systematic structural modifications in the photochemistry of phthalimides are under way.

Experimental

All melting points are uncorrected. IR and UV spectra were recorded on a Shimadzu IR-400 and a Hitachi Model-124 spectrophotometer, respectively. NMR spectra were measured with a Hitachi R-24 spectrometer (60 MHz) and chemical shifts were given on δ (ppm) scales with tetramethylsilane as an internal standard. UV irradiation was carried out in a Pyrex vessel at room temperature, using a Eikosha 500 W high-pressure mercury lamp.

N-(5,6,7,8-Tetrahydro-1-naphthyl)phthalimide (**3**)——A mixture of phthalic anhydride (1.48 g, 0.01 mol) and 5,6,7,8-tetrahydro-1-naphthylamine (1.53 g, 0.0104 mol) was heated in an oil bath at 160—165° for 2.5 hr. The benzene solution of the reaction mixture was decolorized by filtration through short silica gel column and concentrated. Recrystallization of the resulting solid from ethanol afforded almost colorless needles, mp 149—151°, 2.463 g (89%). *Anal.* Calcd. for $C_{18}H_{15}NO_2$: C, 78.00; H, 5.42; N, 5.06. Found: C, 78.25; H, 5.40; N, 5.23. IR ν_{max}^{Nujol} cm^{-1}: 1768, 1750, 1710 (imide C=O). UV λ_{max}^{EtOH} nm (ε): 274 (2150), 293 (1960), 300 (1840). NMR ($CDCl_3$) δ: 1.6—2.0 (4H, C_6– and C_7–H), 2.53 (2H, C_5–H), 2.84 (2H, C_8–H), 6.9—7.2 (3H, aromatic protons), 7.6—8.0 (4H, aromatic protons).

5,10,11,12,12a,12b-Hexahydro-12b-hydroxyisoindolo[2,1-*a*]benz[*cd*]indol-5-one (4)——554 mg of 3 in 300 ml of acetone was irradiated with 500 W high-pressure mercury lamp for 25 min under a nitrogen atmosphere. Evaporation of the solvent gave solid which was recrystallized from ethanol to give colorless prisms, mp 254—256°, 425 mg (77%). *Anal.* Calcd. for $C_{18}H_{15}NO_2$: C, 78.00; H, 5.42; N, 5.06. Found: C, 77.93; H, 5.44; N, 5.18. IR ν_{max}^{Nujol} cm^{-1}: 3300 (OH), 1677 (C=O). UV λ_{max}^{EtOH} nm (ε): 230 (11110), 237 (sh, 10810), 284 (1910), 297 (5340). NMR (pyridine-d_5) δ: 3.06 (1H, C_{12a}–H), 9.00 (1H, O–H).

5,10,11,12-Tetrahydroisoindolo[2,1-*a*]benz[*cd*]indol-5-one (5)——Suspension of 4 (400 mg) in conc. HCl–EtOH (1: 10, v/v, 44 ml) was heated under refluxing for 0.5 hr to give a yellow solution. After standing the reaction mixture at room temperature overnight, precipitated yellow needles were collected by filtration (405.2 mg). Purification of the crude product by recrystallization from ethanol afforded bright yellow needles, mp 169—170°, 314.3 mg (83.5%). *Anal.* Calcd. for $C_{18}H_{13}NO$: C, 83.40; H, 5.02; N, 5.41. Found: C, 83.43; H, 4.95; N, 5.44. IR ν_{max}^{Nujol} cm^{-1}: 1714 (C=O). UV λ_{max}^{EtOH} nm (ε): 235 (28890), 242 (sh, 27220), 277 (30830), 294 (14720), 307 (16560), 370 (8890). NMR ($CDCl_3$) δ: 1.93—2.23 (2H, C_{11}–H), 2.72—2.98 (4H, C_{10}– and C_{12}–H), 6.8—7.7 (7H, aromatic protons).

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Studies on Ketene and Its Derivatives. LXXXVII.[1] Photoreaction of Diketene with 3-Acetoxy-5,5-dimethyl-2-cyclohexenone

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Photoreaction of diketene with 3-acetoxy-5,5-dimethyl-2-cyclohexenone (1) gives 6-acetoxy-7-hydroxy-4,4-dimethyl-*cis*-bicyclo[4.2.0]octan-2-one-7-acetic acid β-lactone (2 and 3). Treatment of 2 with dimethylamine affords 3-acetoxy-7-hydroxy-N,N,4,4-tetramethyl-*cis*-bicyclo[4.2.0]octan-2-one-7-acetamide (4), while similar treatment of 3 affords 1-acetoxy-N,N,4,4-tetramethylcyclooctane-2,6-dione-1-acetamide (5). This result suggests the spiro-configuration of 2 is the *trans* (acetoxy and oxetane O), while that of 3 being the *cis*.

Keywords——photoreaction; diketene; bicyclo[4.2.0]octane derivative; spiro compounds; acyl migration; configuration; shift reagent

In the preceeding paper[1] we have reported that photolysis of a solution of diketene and dimedone resulted in the [2+2]cycloaddition reaction accompanied with ring expansion to give the cyclooctane derivative. We now report the similar reaction of diketene with dimedone monoacetate, 3-acetoxy-5,5-dimethyl-2-cyclohexenone (1), to give the stereoisomers of the bicyclo[4.2.0]octanone, 2 and 3.

Irradiation of a solution of compound 1 and diketene in ethanol or acetonitrile gave crystalline products 2 and 3, to which we assigned the *cis*-bicyclo[4.2.0]octan-2-one-7-acetic acid β-lactone structures, where the juncture of acetoxy and oxetane oxygen of 2 is the *trans* while that of 3 is the *cis* configuration.

Namely, the infrared (IR) spectrum of 2 showed the β-lactone (1830 cm^{-1}), ester (1740 cm^{-1}), and ketone (1700 cm^{-1}) carbonyl absorptions. Nuclear magnetic resonance (NMR) spectrum showed three singlet methyl signals (0.97, 1.10 and 2.07 ppm), three singlet methylene signals (2.24, 2.58, and 3.32 ppm), and a multiplet signal (2.24—2.70 ppm, 3H) which was assignable to C_1-proton and C_8-methylene protons.

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2) Location: *Aobayama, Sendai, 980, Japan.*