Intramolecular [2 + 2]Photocycloadditions of 1-(ω-Alkenyl)-2-pyridones Possessing an Ester Group on the Olefinic Carbon Chain

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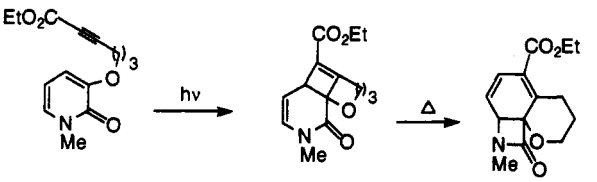
Photochemical reactions of three kinds of 1-(ω-alkenyl)-2-pyridones 1-8 were investigated. Photosensitized cycloadditions of 1-(ω-alkenyl)-2-pyridones and 1,3-bis(ω-alkenyl)-2-pyridone 2-6 afforded intramolecular [2 + 2]cycloadducts across the 5,6-bonds of the 2-pyridones to give the tricyclic lactams 14-18: the additions were site-, regio-, and stereospecific. The yields of the adducts diminished in proportion to increased side-chain length. The one possessing the shortest alkenyl group, 1, and the 1-[ω-(acryloyloxy)alkyl]-2-pyridones 7 and 8, however, gave no products. On the other hand, direct irradiation of 3 afforded a bicyclic lactam 19. The intramolecular cycloaddition mechanism was discussed in terms of the excited state of 2-pyridone, as calculated by the MNDO-CI method.

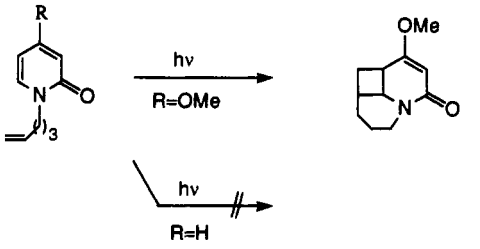
Intramolecular [2 + 2]photocycloadditions of conjugated enones have been widely developed because these are one of the most powerful methods to synthesize a variety of stereocontrolled compounds including natural products.[1] We have investigated photoaddition reactions of singlet and triplet 2-pyridones, which are typical heterocyclic α,β,γ,δ-unsaturated carbonyl compounds.[2] We also previously reported that a new type of tricyclic β-lactam was synthesized by using intramolecular [2 + 2]photocycloaddition of 2-pyridone having an alkynyl carbon chain (Scheme I).[3] On the other hand, photocycloadditions of 2-pyridones possessing an alkenyl carbon chain have been studied, but the reactions have been limited to pyridones having unsubstituted olefinic carbon chain (Scheme II).[4]

In this paper, we describe the intramolecular [2 + 2]-photocycloadditions of 1-(ω-alkenyl)-2-pyridones possessing an electron-poor olefinic moiety. They provide a simple route to tricyclic lactams. We also analyze the regioselectivity of the cycloadditions using the MNDO-CI method.

Scheme I



Scheme II



Results and Discussion

Preparation of Substrates. All of the substrates required for this study were prepared as shown in Scheme III. Dehydrobromination reactions of 2-pyridone (P) or 2,3-dihydroxypyridine with alkenyl bromides provided 1-(ω-alkenyl)-2-pyridones 1 and 3-6. Wittig reaction of 1-(formylethyl)-2-pyridone (9) with ethyl diethylphosphonoacetate gave 2, and dehydrochlorination reactions of 1-(hydroxyalkyl)-2-pyridones 13a,b with acryloyl chloride afforded 7 and 8.

Photochemical Results. A solution of 2 (7.2 mM) in acetonitrile in the presence of benzophenone as a sensitizer was irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter. The reaction was followed by TLC. After removal of solvent, the residue was chromatographed on silica gel to give a single photoadduct 14 in 95% yield. Photosensitized irradiations of 3-6 in acetonitrile afforded also 15-18 in 50%, 27%, 8%, and 26% yields, respectively (Scheme IV). The yields showed a tendency to diminish as the chain length of the alkenyl group became longer. On the other hand, photoirradiation of 3 without benzophenone gave bicyclic lactam 19 in 96% yield.

The structures of 14-18 were assigned as intramolecular [2 + 2]cycloadducts from the spectroscopic evidence. For example, 15, ethyl 5-oxo-6-azatricyclo[4.4.1^{2,10}.0]undec-3-ene-endo-11-carboxylate, showed a strong carbonyl absorption at 1730 cm^{-1} in the IR spectrum for unconjugated ester group. The regiochemistry of 15 was confirmed from the 2D ^{1}H COSY spectum by considering the correlation between methylene protons and cyclobutane protons. The stereochemistry was confirmed by noting the magnitude of the NOE for cyclobutane protons (Figure 1). The stereochemistry of 16 and 17 was also verified by NOE measurements. Compound 19 was confirmed to be 2-[[5-(ethoxycarbonyl)-*trans*-4-pentenyl]oxy]-2-azabicyclo-[2.2.2]hex-5-en-3-one from comparison of the ^{1}H NMR spectrum with that of the related compound 22.[3]

On the basis of these results as shown in Scheme IV, photocycloaddition of the 1-(ω-alkenyl)-2-pyridones was found to be site-, regio-, and stereospecific, and to be dependent on the alkenyl chain length. The intramolecular cycloaddition of 1-(ω-alkenyl)-2-pyridones was found to require the presence of two to five methylene units in the side chain of the chromophore; 1 gave no cycloadduct. The [2 + 2]cycloadditions are triplet processes of the 2-pyridones. On the other hand, the valence isomerization reaction of 3 is ascribed to the singlet excited state of the 2-pyridone, as it is formed only on direct irradiation.

Since the photocycloaddition of 1-(ω-alkenyl)-2-pyridones 2-5 gave 14-17 (Scheme IV) and that of 3-(ω-alkynyl)-2-pyridone[3] (Scheme I) afforded a single adduct

(1) (a) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453. (b) Sato, M.; Abe, Y.; Kaneko, C. *Heterocycles* **1990**, *30*, 217.
(2) (a) Somekawa, K.; Izumi, R.; Taniguchi, K.; Suishu, T.; Tokita, S. Nippon Kagaku Kaishi **1990**, 271. (b) Somekawa, K.; Okumura, Y.; Uchida, K.; Shimo, T. *J. Heterocycl. Chem.* **1988**, *25*, 731.
(3) Somekawa, K.; Oda, H.; Shimo, T. *Chem. Lett.* **1991**, 2077.
(4) Kaneko, C.; Uchiyama, K.; Sato, M.; Katagiri, N. *Chem. Pharm. Bull.* **1986**, *34*, 3658.

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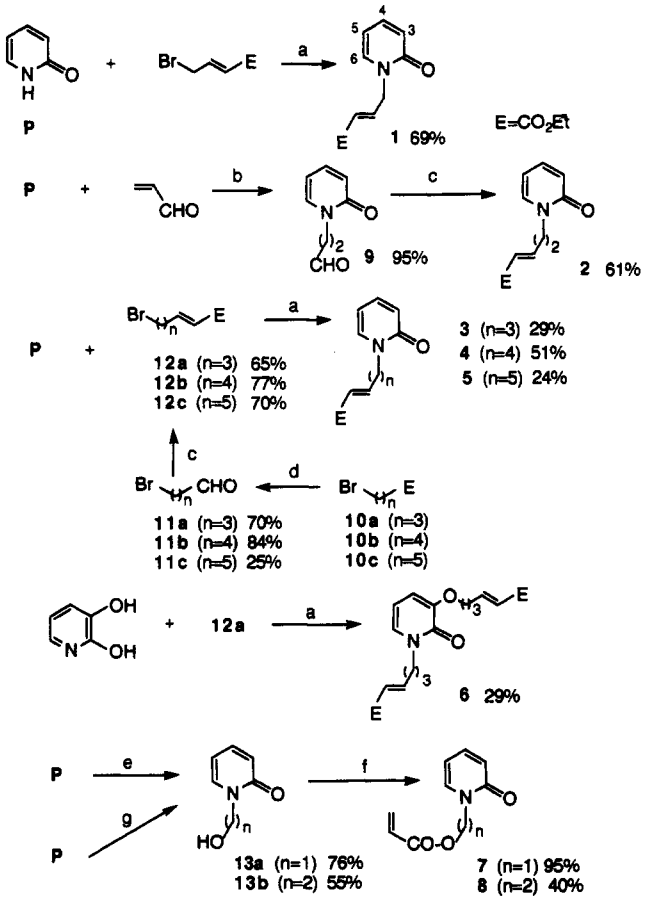
Scheme III[a]



[a] Conditions: (a) K_2CO_3, acetone; (b) 120 °C, C_6H_6; (c) NaH, $(EtO)_2POCH_2CO_2Et$, THF; (d) DIBALH, toluene; (e) *p*-formaldehyde, 100 °C; (f) acryloyl chloride, Et_3N, CH_3CN; (g) 2-bromoethanol, K_2CO_3, acetone.

Scheme IV

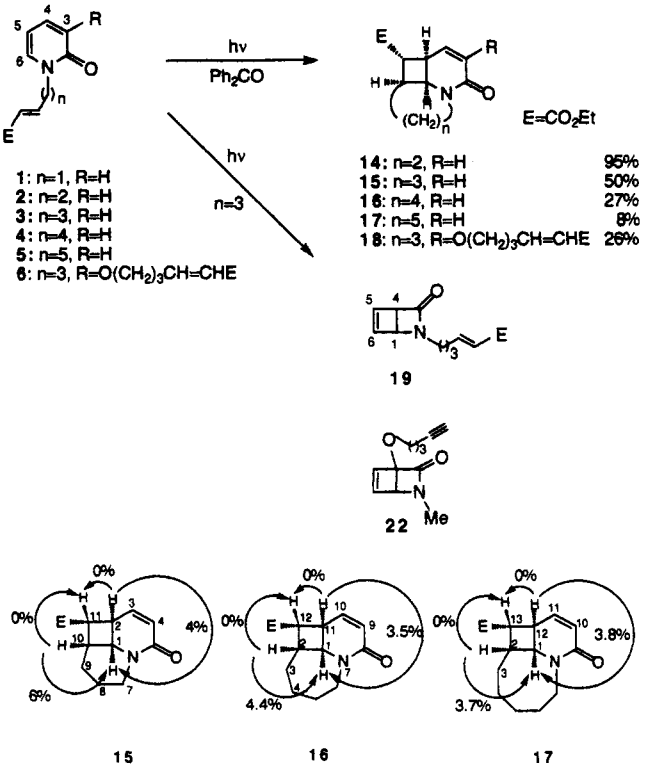


Figure 1. NOE measurements of photocycloadducts 15–17.

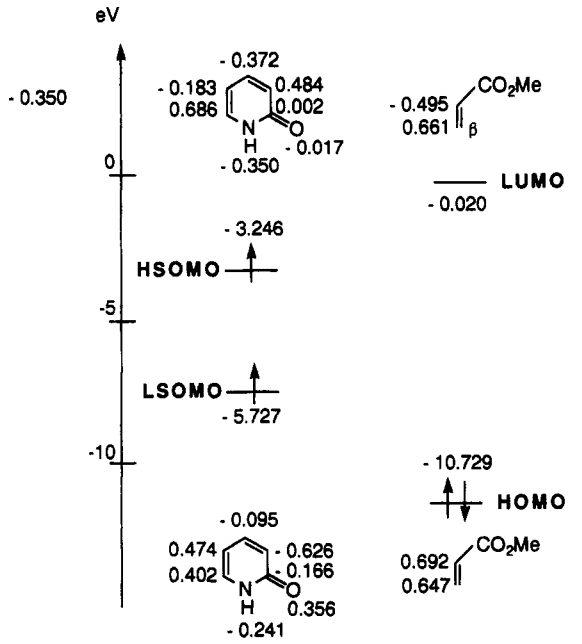


Figure 2. Estimated energies and coefficients of 2-pyridone and methyl acrylate.

across the C_3–C_4 double bond in 2-pyridone, photoirradiation of 1,3-bis(ω-alkenyl)-2-pyridone **6** was carried out in order to clarify the reactivity of the two kinds of double bonds of the 2-pyridone ring. The reactivity of the C_5–C_6 double bond was found to be higher than that of the C_3–C_4 double bond from the fact that **6** gave **18**. The reactivity of the C_3–C_4 position is inferred to be reduced owing to the initial bond formation at the C_5–C_6 position.

We now describe a MNDO-CI treatment of the photocycloadditions which leads to an understanding of these specificities. The MNDO-CI method has become an increasingly powerful tool for the understanding of cycloaddition reactions.[5] It is reasonable to assume that these intramolecular cycloadditions proceed via biradical intermediates of the 2-pyridones. The orbital energies and coefficients of the triplet excited state (HSOMO and LSOMO) for 2-pyridone and that of frontier orbitals (LUMO and HOMO) for methyl acrylate were obtained by a method similar to that used in the case of the 4-(ω-alkenyloxy)-6-methyl-2-pyrones.[5b] It is reasonable to consider that the mechanism of the intramolecular cycloaddition of **2–6** is similar to that of the reaction between 2-pyridone and methyl acrylate. Figure 2 shows the estimated orbital energies and coefficients for 2-pyridone and methyl acrylate obtained from the MNDO-CI method.[6]

The energy gap (ΔE) between HSOMO(2-pyridone)–LUMO(methyl acrylate) is smaller than LSOMO(2-pyridone)–HOMO(methyl acrylate), and this frontier orbital interaction is much more important in the photocycloaddition of **2–6**. As the coefficients at C_6 in HSOMO of 2-pyridone and that at C_β in the LUMO orbital of methyl acrylate are larger than any other positions, the initial bond formation is deduced to occur at C(6)–C(β) to give a biradical intermediate **A** which may yield the adducts **14–18** (Scheme V). The regiochemistry was also suggested from the consideration of the atomic charge between 2-pyridone and methyl acrylate calculated by the

(5) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Shimo, T.; Tajima, J.; Suishu, T.; Somekawa, K. *J. Org. Chem.* **1991**, *56*, 7150.

(6) Dewar, M. J. S. QCPE **1989**, *581*, MOPAC Version 5.0.

Scheme V

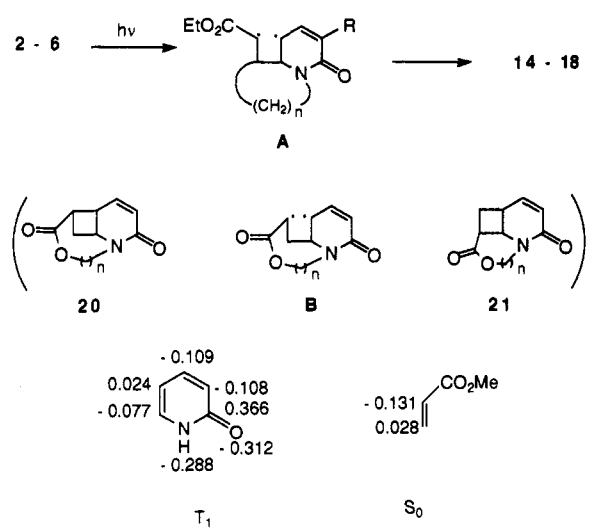


Figure 3. Calculated atomic charges of excited triplet 2-pyridone (T_1) and that of the ground state of methyl acrylate (S_0).

MNDO-CI method (Figure 3).

The lack of intramolecular [2 + 2]cycloadducts **20** (cross adduct) and **21** (parallel adduct) from irradiation of **7** and **8** in Scheme V may be considered as follows. The approach between two olefinic moieties for **20** would be disturbed by the restricted rotation of the inner-enone part (**2–6**: outer-enone) owing to the short and conjugated carbonyl system in the side chain, and a possible biradical intermediate **B** in Scheme V might be also unstable because of the rigid structure of the dihydro-2-pyridone ring. The approach for **21** would be unfavorable for the frontier orbital interaction in Figure 2. The longer chains in **7** and **8** seem to tell us that unfavorable entropy effect of the anticipative intermediates in the larger rings hardly gives intramolecular photoadducts as shown in the longer chains of **2–6** system.

These regioselective intramolecular reactions of N-substituted 2-pyridones are very similar to those of 4-substituted 2-pyrones,[5b] but different from those of enones.[7] Intermolecular photoadditions of those dienones were however not so similar.[2a,8] The photoadditions of dienones may be very sensitive to the reaction system and condition.

Experimental Section

All melting points are uncorrected. ^{1}H NMR spectra were determined with a JEOL JNM-GSX400 (400-MHz) spectrometer (tetramethylsilane as an internal standard), and ^{13}C NMR spectra were measured at 100.5 MHz on the JEOL JNM-GSX400 instrument using $CDCl_3$ as internal reference. IR spectra were recorded with a JASCO A-3 spectrometer. Low-resolution mass spectral data were obtained with a JMS-OISG instrument at 70 eV. Photoirradiation was carried out in a Pyrex tube by using a Riko 400W high-pressure mercury lamp; a merry-go-round apparatus was used, and the light was passed through a UV 35 filter (Toshiba) which cuts off at $\lambda \leq 350$nm.

1-[3-(Ethoxycarbonyl)-2-*trans*-propenyl]-2-pyridone (1). To a solution of 2-pyridone (P) (0.50 g, 5.0 mmol) containing potassium carbonate (1.47 g, 10.6 mmol) in acetone (20 mL) was added ethyl 4-bromocrotonate (1.56 g, 10.0 mmol), and the solution was refluxed for 18 h. After filtration of the reaction mixture, the solvent was removed in vacuo and then the resulting residue was submitted to column chromatography (silica gel, chloroform) to give 1 (0.76 g, 69%) as a colorless oil: IR (neat) 1720, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.26 (3 H, $CO_2CH_2CH_3$), 4.00–4.20 (4 H, m, CH_2, $CO_2CH_2CH_3$), 5.76 (1 H, d, J = 16.0 Hz, =CH), 6.19 (1 H, t, J = 8.0 Hz, 5-H), 6.56 (1 H, d, J = 8.0 Hz, 3-H), 6.91 (1 H, m, =CH), 7.10–7.45 (2 H, m, 4-, 6-H); mass spectrum m/z (relative intensity) 207 (M^+, 58), 134 (100). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.74. Found: C, 63.52; H, 6.13; N, 6.51.

1-[4-(Ethoxycarbonyl)-3-*trans*-butenyl]-2-pyridone (2). (1) A solution of P (2.0 g, 21 mmol) and acrolein (1.77 g, 31.5 mmol) in benzene (20 mL) was heated at 120 °C in a sealed tube for 22 h. After removal of the solvent, the residue was chromatographed (silica gel, chloroform) to give **9** (2.99 g, 95%) as a colorless oil: IR (neat) 1710, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.95, 4.12 (each 2 H, t, J = 6.0 Hz, NCH_2CH_2), 6.08 (1 H, t, J = 6.0 Hz, 5-H), 6.46 (1 H, d, J = 6.0 Hz, 3-H), 7.16–7.48 (2 H, m, 4-, 6-H), 9.75 (1 H, s, CHO); mass spectrum m/z (relative intensity) 151 (M^+, 24), 123 (100). Anal. Calcd for $C_8H_9NO_2$: C, 62.26; H, 6.13; N, 8.60. Found: C, 62.56; H, 6.00; N, 8.27.

(2) To a dry THF (100 mL) suspension of sodium hydride (0.45 g, 19.0 mmol) at room temperature under nitrogen atmosphere was added ethyl diethylphosphonoacetate (4.1 mL, 19.0 mmol) followed by a THF (7 mL) solution of **9** (2.87 g, 19.0 mmol). The solution was stirred for 3.5 h. After being quenched with water (30 mL), the aqueous layer was extracted with chloroform (5 × 40 mL). The combined organic layer was concentrated and column chromatographed (silica gel, chloroform) to afford **2** (2.56 g, 61%) as a colorless oil: IR (neat) 1720, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (3 H, $CO_2CH_2CH_3$), 2.70 (2 H, q, CH_2), 4.00–4.20 (4 H, m, NCH_2, $CO_2CH_2CH_3$), 5.88 (1 H, d, J = 16.0 Hz, =CH), 6.18 (1 H, t, J = 8.0 Hz, 5-H), 6.56 (1 H, d, J = 8.0 Hz, 3-H), 6.80–7.00 (1 H, m, =CH), 7.10–7.45 (2 H, m, 4-, 6-H); mass spectrum m/z (relative intensity) 221 (M^+, 34), 95 (100). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 64.88; H, 6.59; N, 6.17.

1-[5-(Ethoxycarbonyl)-4-*trans*-pentenyl]-2-pyridone (3). (1) To a solution of ethyl 4-bromobutanoate (**10a**) (31.2 g, 160 mmol) in dry toluene (850 mL) under nitrogen atmosphere was slowly added DIBALH (25.0 g, 171 mmol, 1.5 M toluene solution) at −78 °C. After this solution was stirred for 3 h at −78 °C, 5% hydrochloric acid solution (100 mL) was added at room temperature. The organic layer was separated, washed with water, and dried ($MgSO_4$) to give crude **11a** (17.0 g, 70%), which was used directly for the next step because it decomposed upon column chromatography: IR (neat) 1720 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.17, 2.65, 3.45 (each 2 H, CH_2), 9.79 (2 H, s, CHO).

(2) To a dry THF (340 mL) suspension of sodium hydride (2.7 g, 113 mmol) at room temperature under nitrogen atmosphere was added ethyl diethylphosphonoacetate (25.3 g, 113 mmol) followed by a THF (20 mL) solution of **11a** (17.0 g, 113 mmol). The solution was stirred for 1.5 h. After being quenched into water (80 mL), the aqueous layer was extracted with chloroform (5 × 80 mL). The combined organic layer was concentrated to give crude **12a** (16.2 g, 65%), which was used for the next step without further purification: IR (neat) 1710, 1650 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.29, 4.18 (CO_2Et), 2.02, 2.38, 2.42 (each 2 H, CH_2), 5.88 (1 H, d, J = 15.8 Hz, =CH), 6.91 (1 H, dt, J = 15.8, 7.4 Hz, =CH); mass spectrum m/z (relative intensity) 220 (M^+, 35), 177 (100).

(3) To a solution of P (2.90 g, 30.0 mmol) containing potassium carbonate (5.4 g, 36.0 mmol) in acetone (100 mL) was added **12a** (8.0 g, 36.0 mmol), and the solution was refluxed for 15 h. After filtration of the reaction mixture, the solvent was removed and then the resulting residue was column chromatographed (silica gel, ethyl acetate) to afford **3** (2.09 g, 29%) as a colorless oil: IR (neat) 1720, 1660 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.23, 4.18 (CO_2Et), 1.95, 2.28, 3.95 (each 2 H, CH_2), 5.86 (1 H, dt, J = 15.8, 0.7 Hz, =CH), 6.16 (1 H, dt, J = 6.3, 0.8 Hz, 5-H), 6.56 (1 H, d, J = 9.2 Hz, 3-H), 6.94 (1 H, dt, J = 7.0, 15.8 Hz, =CH), 7.24 (dd, J = 6.3, 0.8 Hz, 6-H), 7.31 (1 H, m, 4-H); ^{13}C NMR ($CDCl_3$) δ 14.1, 27.3, 28.9, 49.1, 60.1, 106.0, 121.0, 122.1, 137.3, 139.3, 147.0, 162.4, 166.2; mass spectrum m/z (relative intensity) 235 (M^+, 17), 67 (100). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.38; H, 7.23; N, 5.96. Found: C, 66.21; H, 7.05; N, 5.88.

1-[6-(Ethoxycarbonyl)-5-*trans*-hexenyl]-2-pyridone (4). (1) To a solution of ethyl 5-bromopentanoate (**10b**) (10.0 g, 47.8 mmol) in dry toluene (260 mL) under nitrogen atmosphere was slowly added DIBALH (50.6 mL, 52.6 mmol) at −78 °C. After

(7) Pirrung, M. C.; Webster, N. J. G. *J. Org. Chem.* **1987**, *52*, 3603.
(8) Somekawa, K.; Shimo, T.; Suishu, T. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 354.
(9) Cilag Ltd. Swiss Patent No. 243101 (16 November 1946); Chem. Abs., **1949**, *43*, 7973.

the solution was stirred for 3 h at −78 °C, 5% hydrochloric acid solution (150 mL) was added at room temperature. The organic layer was separated, washed with water, and dried ($MgSO_4$) to give crude **11b** (6.65 g, 84%), which was used for the next step without further purification: IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80, 1.90, 2.49, 3.42 (each 2 H, CH_2), 9.78 (1 H, s, CHO).

(2) To a dry THF (130 mL) suspension of sodium hydride (0.95 g, 39.0 mmol) under nitrogen atmosphere was added ethyl diethylphosphonoacetate (8.82 g, 39.0 mmol) followed by **11b** (6.5 g, 39.0 mmol). The solution was stirred for 2 h. After being quenched by water (80 mL), the aqueous layer was extracted with chloroform (5 × 30 mL). The combined organic layer was concentrated to give crude **12b** (9.1 g, 77%), which was used for the next step without further purification: IR (neat) 1710, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 4.19 (CO_2Et), 1.64, 1.89, 2.24, 3.41 (each 2 H, CH_2), 5.84 (1 H, d, J = 15.8, =CH), 6.94 (1 H, dt, J = 15.8, 7.0, =CH); mass spectrum m/z (relative intensity) 236 (M + 1, 4), 55 (100).

(3) To a solution of P (2.2 g, 23.0 mmol) containing potassium carbonate (3.83 g, 27.6 mmol) in acetone (100 mL) was added **12b** (6.53 g, 27.6 mmol), and the solution was refluxed for 56 h. After filtration of the reaction mixture, the solvent was removed and then the resulting residue was column chromatographed (silica gel, ethyl acetate) to give **4** (2.91 g, 51%) as a colorless oil: IR (neat) 1720, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28, 4.18 (CO_2Et), 1.52, 1.76, 2.25, 3.94 (each 2 H, CH_2), 5.82 (1 H, dt, J = 15.8, 0.7 Hz, =CH), 6.16 (1 H, dt, J = 6.3, 0.7 Hz, 5-H), 6.56 (1 H, d, J = 9.2 Hz, 3-H), 6.92 (1 H, dt, J = 15.7, 0.7 Hz, =CH), 7.24 (1 H, dd, J = 6.3, 0.9 Hz, 6-H), 7.30 (1 H, m, 4-H); ^{13}C NMR ($CDCl_3$) δ 14.0, 24.9, 28.6, 31.5, 49.3, 60.0, 105.7, 120.9, 121.7, 137.4, 139.2, 148.0, 162.4, 166.3; mass spectrum m/z (relative intensity) 249 (M^+, 31) 96 (100). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.50; H, 7.63; N, 5.62. Found: C, 67.36; H, 7.50; N, 5.72.

1-[7-(Ethoxycarbonyl)-6-*trans*-heptenyl]-2-pyridone (5). (1) A solution of 6-bromohexanoic acid (25.0 g, 128 mmol) and p-toluenesulfonic acid (2.2 g, 12.8 mmol) in methanol (17.7 g, 550 mmol) was refluxed for 6 d. The organic layer was separated, dried ($MgSO_4$), and concentrated to give crude **10c** (26.7 g, 94%), which was used for the next step: IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.48, 1.66, 1.88, 2.34, 3.41 (each 2 H, CH_2), 3.68 (3 H, s, Me).

(2) To a solution of **10c** (16.8 g, 80.0 mmol) in dry toluene (400 mL), was slowly added DIBALH (88.9 mL, 92.4 mmol) at −78 °C. After the solution was stirred for 3 h at −78 °C, 5% hydrochloric acid solution (180 mL) was added at room temperature. The organic layer was separated, washed with water, and dried ($MgSO_4$) to give crude **11c** (3.65 g, 25%), which was used for the next step: IR (neat) 1720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.39, 1.66, 1.89, 2.46, 3.41 (each 2 H, CH_2), 9.77 (1 H, s, CHO).

(3) To a dry THF (60 mL) suspension of sodium hydride (0.48 g, 20 mmol) under nitrogen atmosphere was added ethyl diethylphosphonoacetate (4.5 g, 20 mmol) followed by **11c** (3.6 g, 20 mmol). The solution was stirred for 3 h. After being quenched with water (100 mL), the aqueous layer was extracted with chloroform (3 × 30 mL). The combined organic layer was concentrated to give crude **12c** (3.5 g, 70%), which was used for the next step: IR (neat) 1720, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 4.18 (CO_2Et), 1.49, 1.59, 1.86, 2.22, 3.41 (each 2 H, CH_2), 5.82 (1 H, d, J = 15.4 Hz, =CH), 6.95 (1 H, dt, J = 15.4, 7.0 Hz, =CH); mass spectrum m/z (relative intensity) 250 (M + 1, 13), 55 (100).

(4) To a solution of P (1.23 g, 13.0 mmol) containing potassium carbonate (1.98 g, 14.1 mmol) in acetone (40 mL) was added **12c** (4.0 g. 15.6 mmol), and the solution was refluxed for 3 d. After filtration of the reaction mixture, the solvent was refluxed for 3 d. After filtration of the reaction mixture, the solvent was removed and then the resulting residue was column chromatographed (silica gel, ethyl acetate) to give **5** (0.80 g, 24%) as a colorless oil: IR (neat) 1720, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 4.18 (CO_2Et), 1.38, 1.51, 1.77, 2.21, 3.93 (each 2 H, CH_2), 5.80 (1 H, dt, J = 15.8, 0.7 Hz, =CH), 6.17 (1 H, dt, J = 6.3, 0.7 Hz, 5-H), 6.54 (1 H, d, J = 9.2 Hz, 3-H), 6.93 (1 H, dt, J = 15.8, 7.0 Hz, 5-H), 7.30 (2 H, m, 4-, 6-H); ^{13}C NMR ($CDCl_3$) δ 14.2, 26.0, 27.6, 28.9, 31.8, 49.7, 60.1, 105.8, 121.1, 121.5, 137.4, 139.2, 148.6, 162.4, 166.3; mass spectrum m/z (relative intensity) 263 (M^+, 21), 95 (100). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.44; H, 7.98; N, 5.32. Found: C, 68.62; H, 7.76; N, 5.07.

1-[5-(Ethoxycarbonyl)-*trans*-4-pentenyl]-3-[[5-(ethoxycarbonyl)-*trans*-4-pentenyl]oxy]-2-pyridone (6). To a solution of 2,3-dihydroxypyridine (1.9 g, 17 mmol) containing potassium carbonate (6.1 g, 42.5 mmol) in acetone (40 mL) was added **12a** (7.6 g, 34 mmol), and the solution was refluxed for 43 h. After filtration of the reaction mixture, the solvent was removed and the resulting residue was column chromatographed (silica gel, ethyl acetate) to give **6** (1.92 g, 29%) as a colorless oil: IR (neat) 1720, 1650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28, 4.18 (CO_2Et), 1.95, 2.03, 2.27, 2.44 (each 2 H, CH_2), 3.96 (4 H, NCH_2, OCH_2), 5.87 (2 H, d, J = 15.8 Hz, =CH), 6.09 (1 H, t, J = 8.7 Hz, 5-H), 6.62 (1 H, d, J = 8.7 Hz, 4-H), 6.82 (1 H, d, J = 8.7 Hz, 6-H), 6.92 (2 H, m, =CH); ^{13}C NMR ($CDCl_3$) δ 14.4, 27.5, 28.7, 29.3, 49.4, 60.4, 67.9, 105.0, 114.0, 122.3, 128.7, 147.4, 148.0, 161.8, 166.4; mass spectrum m/z (relative intensity) 391 (M^+, 24), 111 (100). Anal. Calcd for $C_{21}H_{29}NO_6$: C, 64.45; H, 7.42; N, 3.58. Found: C, 64.27; H, 7.65; N, 3.39.

1-[(Acryloyloxy)methyl]-2-pyridone (7). (1) A mixture of P (18.8 g, 200 mmol) and paraformaldehyde (6.4 g, 210 mmol) was heated at 100 °C for 0.5 h in a sealed tube. The reaction mixture was recrystallized from chloroform to give **13a** (18.7 g, 76%, mp 80–83 °C (lit.[7] mp 86 °C)).

(2) To a solution of **13a** (1.02 g, 10.7 mmol) containing triethylamine (1.25 g, 12.4 mmol) in acetonitrile (3 mL) was added acryloyl chloride (1.09 g, 12.0 mmol). The solution was stirred at room temperature for 3 h. After filtration of the reaction mixture, the solvent was removed and then the resulting residue was submitted to column chromatography (silica gel, chloroform) to give **7** (1.38 g, 95%) as a colorless oil: IR (neat) 1730, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.80–6.60 (5 H, m, 3-, 5-H, =CH, $=CH_2$), 5.92 (2 H, s, CH_2), 7.30 (1 H, t, J = 7.0 Hz, 4-H), 7.54 (1 H, d, J = 7.0 Hz, 6-H); mass spectrum m/z (relative intensity) 179 (M^+, 82), 121 (100). Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.58; H, 4.98; N, 7.59.

1-[(Acryloyloxy)ethyl]-2-pyridone (8). (1) To a solution of P (1.02 g, 11.0 mmol) containing potassium carbonate (2.16 g, 16.0 mmol) in acetone (30 mL) was added 2-bromoethanol (2.61 g, 22.0 mmol), and the solution was refluxed for 12 h. After filtration of the reaction mixture, the solvent was removed, and then the resulting residue was chromatographed (silica gel chloroform) to give **13b** (0.82 g, 55%): mp 95–97 °C; IR (KBr) 3300, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.70–4.30 (5 H, m, CH_2, OH), 6.23 (1 H, t, J = 10.0 Hz, 5-H), 6.56 (1 H, d, J = 12.0 Hz, 3-H), 7.20–7.56 (2 H, m, 4-, 6-H); mass spectrum m/z (relative intensity) 139 (M^+, 20), 96 (100). Anal. Calcd for $C_7H_9NO_2$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.43; H, 6.46; N, 10.03.

(2) To a solution of **13b** (3.0 g, 21.6 mmol) containing triethylamine (2.50 g, 24.8 mmol) in acetonitrile (6 mL) was added acryloyl chloride (2.18 g, 24.1 mmol), and the same procedure described for **7** afforded **8** (1.66 g, 4%) as a colorless oil: IR (neat) 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.27, 4.52 (each 2 H, CH_2), 5.80–6.50 (4 H, m, 5-H, $=CH_2$, =CH), 6.70 (1 H, d, J = 10.0 Hz, 3-H), 7.10–7.40 (2 H, m, 4-, 6-H); mass spectrum m/z (relative intensity) 193 (M^+, 23), 55 (100). Anal. Calcd for $C_{10}H_{11}NO_3$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.31; H, 5.88; N, 7.13.

Ethyl 5-Oxo-6-azatricyclo[4.3.1^{2,9}.0]dec-3-ene-*endo*-10-carboxylate (14). A solution of **2** (100 mg, 0.45 mmol) and benzophenone (20 mg, 0.11 mmol) as a sensitizer in acetonitrile (60 mL) under nitrogen atmosphere was irradiated for 1 h. The solvent was removed, and the residual liquid was submitted to column chromatography (silica gel, ethyl acetate) to afford **14** (95 mg, 95%) as a colorless oil: IR (neat) 1730, 1655 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25, 4.17 (CO_2Et), 1.84 (1 H, ddt, J = 15.0, 9.0, 2.1 Hz, 8-H), 2.10 (1 H, m, 8-H'), 2.95 (1 H, t, J = 7.8 Hz, 10-H), 3.10 (3 H, m, 2-, 7-, 9-H), 4.07 (1 H, t, J = 7.1 Hz, 1 H), 4.45 (1 H, ddd, J = 15.0, 9.0, 3.0 Hz, 7-H'), 5.64 (1 H, d, J = 10.0 Hz, 4-H), 6.46 (1 H, dd, J = 10.0, 6.5 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ 14.1, 28.4, 30.5, 41.4, 45.9, 53.4, 56.6, 60.9, 125.5, 137.7, 163.1, 172.9; mass spectrum m/z (relative intensity) 221 (M^+, 33), 95 (100). Anal. Calcd for $C_{12}H_{15}NO_3$: C, 65.14; H, 6.83; N, 6.33. Found: C, 65.28; H, 6.68; N, 6.10.

Ethyl 5-Oxo-6-azatricyclo[4.4.1^{2,10}.0]undec-3-ene-*endo*-11-carboxylate (15). A solution of **3** (602 mg, 2.6 mmol) and benzophenone (158 mg, 0.87 mmol) in acetonitrile (360 mL) was irradiated for 1 h, and the usual workup yielded **15** (301 mg, 50%) as a pale yellow oil: IR (neat) 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$)

δ 1.27, 4.15 (CO_2Et), 1.7 (4 H, m, 8-, 9-CH_2), 2.33 (1 H, dt, J = 12.1, 6.7 Hz, 7-H), 2.77 (1 H, dt, J = 8.7, 5.9 Hz, 10-H), 3.09 (1 H, m, 2-H), 3.31 (1 H, t, J = 8.7 Hz, 11-H), 4.00 (1 H, t, J = 5.9 Hz, 1-H), 4.57 (1 H, bd, J = 12.1 Hz, 7-H'), 5.89 (1 H, d, J = 9.9 Hz, 4-H), 6.45 (1 H, dd, J = 9.9, 6.0 Hz, 3-H); ^{13}C NMR ($CDCl_3$) δ 14.1, 21.8, 23.4, 33.8, 37.8, 39.0, 47.5, 50.8, 60.7, 125.4, 137.7, 162.5, 172.8; mass spectrum m/z (relative intensity) 235 (M^+, 6), 96 (100). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.38, H, 7.23; N, 5.96. Found: C, 66.11; H, 7.02; N, 6.18.

Ethyl 8-Oxo-7-azatricyclo[5.4.1^{2,11}.0]dodec-9-ene-*endo*-12-carboxylate (16). A solution of **4** (822 mg, 3.0 mmol) and benzophenone (200 mg, 1.1 mmol) in acetonitrile (480 mL) was irradiated for 1.5 h, and the usual workup afforded **16** (221 mg, 27%) as a colorless oil: IR (neat) 1730, 1670 cm^{-1}, ^1H NMR ($CDCl_3$) δ 1.27, 4.17 (CO_2Et), 1.55 (1 H, q, J = 12.5 Hz, 3-H), 1.6 (4 H, m, 4-, 5-CH_2), 2.01 (1 H, m, 3-H'), 2.27 (1 H, m, 6-H), (1 H, t, J = 7.3 Hz, 12-H), 2.79 (1 H, m, 2-H), 3.49 (1 H, m, 11-H), 4.2 (1 H, t, J = 10.8 Hz, 1-H), 4.72 (1 H, bd, J = 13.6 Hz, 6-H'), 5.83 (1 H, d, J = 8.8 Hz, 9-H), 6.38 (1 H, dd, J = 8.8, 5.1 Hz, 10-H); ^{13}C NMR ($CDCl_3$) δ 14.3, 27.6, 27.7, 31.7, 32.2, 45.4, 48.8, 51.4, 54.5, 61.0, 123.4, 138.4, 162.0, 173.4; mass spectrum m/z (relative intensity) 249 (M^+, 21), 96 (100). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.50; H, 7.63; N, 5.62. Found: C, 67.33; H, 7.31; N, 5.83.

Ethyl 9-Oxo-8-azatricyclo[6.4.1^{2,12}.0]tridec-10-ene-*endo*-13-carboxylate (17). A solution of **5** (130 mg, 0.50 mmol) and benzophenone (30 mg, 0.16 mmol) in acetonitrile (70 mL) was irradiated for 4 h, and the usual workup gave **17** (10 mg, 8%) as a colorless oil: IR (neat) 1730, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 4.19 (CO_2Et), 1.62–1.83 (8 H, m, 3-, 4-, 5-, 6-CH_2), 2.44 (1 H, dt, J = 13.2, 4.4 Hz, 7-H), 2.52 (1 H, t, J = 3.7 Hz, 7-H), 2.68 (1 H, m, 2-H), 3.51 (1 H, m, 12-H), 4.27 (1 H, t, J = 9.2 Hz, 1-H), 4.48 (1 H, ddd, J = 13.2, 9.9, 4.4 Hz, 7-H'), 5.88 (1 H, dd, J = 9.9, 1.8 Hz, 10-H), 6.39 (1 H, dd, J = 9.9, 4.0 Hz, 11-H); mass spectrum m/z (relative intensity) 263 (M^+, 18), 96 (100). Anal. Calcd for $C_{15}H_{21}NO_3$: C, 68.44; H, 7.98; N, 5.32. Found: C, 68.18; H, 8.20; N, 5.58.

Ethyl 4-[[5-(Ethoxycarbonyl)-*trans*-4-pentenyl]oxy]-5-oxo-6-azatricyclo[4.4.1^{2,10}.0]undec-3-ene-*endo*-11-carboxylate (18). A solution of **6** (2.59 g, 7.0 mmol) and benzophenone (0.40 g, 2.2 mmol) in acetonitrile (1200 mL) was irradiated for 1.5 h, and the usual workup gave **18** (0.67 g, 26%) as a colorless oil: IR (neat) 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29, 4.16 (CO_2Et), 1.69 (4 H, m, 8-, 9-CH_2), 1.94 (2 H, m, CH_2), 2.30 (1 H, m, 7-H), 2.38 (2 H, q, J = 6.6 Hz, CH_2), 3.12 (1 H, m, 2-H), 3.26 (1 H, t, J = 9.9 Hz, 11-H), 3.70 (2 H, t, J = 5.7 Hz, OCH_2), 3.98 (1 H, t, J = 5.6 Hz, 1-H), 4.57 (1 H, d, J = 10.9 Hz, 7-H'), 5.26 (1 H, d, J = 7.0 Hz, 3-H), 5.85 (1 H, d, J = 10.4 Hz, =CH), 6.96 (1 H, m, =CH); mass spectrum m/z (relative intensity) 391 (M^+, 27), 94 (100). Anal. Calcd for $C_{21}H_{29}NO_6$: C, 64.45; H, 7.42; N, 3.58. Found: C, 64.19; H, 7.31; N, 3.65.

2-[[5-(Ethoxycarbonyl)-*trans*-4-pentenyl]oxy]-2-azabicyclo[2.2.2]hex-5-en-3-one (19). A solution of **3** (395 mg, 1.7 mmol) in acetonitrile (240 mL) without benzophenone was irradiated for 10 h, and the usual workup gave **19** (380 mg, 96%) as a colorless oil: IR (neat) 1730, 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.28, 4.15 (CO_2Et), 1.69, 2.24 (each 2 H, CH_2), 3.12, 3.26 (each 1 H, NCH_2), 4.10 (1 H, m, 4-H), 4.34 (1 H, m, 1-H), 5.84 (1 H, d, J = 15.4 Hz, =CH), 6.59 (2 H, m, 5-, 6-H), 6.92 (1 H, dt, J = 15.4, 7.2 Hz, =CH); ^{13}C NMR ($CDCl_3$) δ 14.2, 26.0, 29.5, 42.8, 54.0, 57.5, 60.3, 122.2, 140.5, 141.0, 147.3, 170.6; mass spectrum m/z (relative intensity) 235 (M^+, 2) 52 (100). Anal. Calcd for $C_{13}H_{17}NO_3$: C, 66.38; H, 7.23; N, 5.96. Found: C, 66.09; H, 7.48; N, 6.31.

Extensive Chlorination of Methylnaphthalenes, Friedel–Crafts Alkylation of Pentachlorobenzene by Heptachloro(chloromethyl)naphthalenes, and Related Results

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The chlorination of 2-methylnaphthalene (**1**) and 1-methylnaphthalene (**12**) by means of Silberrad's reagent (initial components: SO_2Cl_2, S_2Cl_2, and $AlCl_3$) has been performed. From **1** or **12**, the following compounds have been synthesized for first time: nonachloro-3-(chloromethyl)-1,4-dihydronaphthalene (**3**), nonachloro-7-(chloromethyl)-1,4-dihydronaphthalene (**4**), perchloro-3-vinylindene (**2**), perchloro-1-vinylindan, nonachloro-4-(chloromethyl)-1,4-dihydronaphthalene (**11**), heptachloro-7-(chloromethyl)naphthalene (**6**), heptachloro-8-(chloromethyl)naphthalene (**10**), heptachloro-7-methylnaphthalene, heptachloro-8-methylnaphthalene, 2-(bromochloromethyl)heptachloronaphthalene, 1-(bromochloromethyl)heptachloronaphthalene, heptachloro-7-formylnaphthalene (**24**), heptachloro-8-formylnaphthalene (**26**), (2-heptachloronaphthyl) (pentachlorophenyl)-methane (**17**), and (1-heptachloronaphthyl) (pentachlorophenyl)methane (**20**). Silberrad's reagent interconverts dihydronaphthalenes **3** and **4**. The $AlCl_3$-promoted Friedel–Crafts alkylation of pentachlorobenzene (**16**) by naphthalenes **6** and **10**, giving diarylmethanes **17** and **20**, respectively, takes place in mild conditions (refluxing CS_2) although the substrate and the alkylating agents are highly crowded polychloro compounds. By heating (100 °C) a mixture of **17**, **16**, and $AlCl_3$, 1*H*-heptachloronaphthalene (**18**) and bis(pentachlorophenyl)methane were obtained. Aldehyde **24**, treated with $Rh(PPh_3)_3Cl$, gave 2*H*-heptachloronaphthalene, which was prepared in pure form for the first time. Under similar treatment, aldehyde **26** gave **18**. The X-ray structures of indene **2** and dihydronaphthalene **11** are reported and discussed. Some probable mechanisms, as well as IR, UV, and ^1H NMR spectra data of the compounds synthesized, are presented.

Introduction

In the context of our investigations on highly chlorinated compounds, we reported the Friedel–Crafts condensation between polychlorobenzenes and highly chlorinated alkylating agents by means of $AlCl_3$.[1] This condensation leads to overcrowded polyphenylmethanes (which are the usual precursors of exceptionally stable radicals[2] and carbanions[2d,f,3]),[1a,c,2h,i] and the relevant method is high-

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