September, 1986] © 1986 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 59, 2811—2818 (1986) 2811

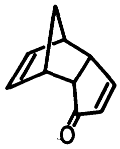
Synthesis and Photolysis of Tricyclo[5.3.1.0^{2,6}]undeca-3,9-dien-8-ones and -4,9-dien-8-ones. Formation of Novel Trishomocubanones[1]

Toshio Ogino* and Kazuyuki Awano*,†
Department of Chemistry, Faculty of Education, Niigata University,
Ikarashi, Niigata 950-21
†Department of Industrial Chemistry, Nagaoka Technical College,
Nishikatagai, Nagaoka 940

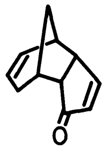
(Received February 14, 1986)

A series of 10-substituted tricyclo[5.3.1.0^{2,6}]undeca-3,9-dien-8-ones (**6**) and the 4,9-dien-8-one isomers (**7**) were synthesized and photolyzed. Upon irradiation, whereas most of the derivatives underwent [2+2] photocyclization to give the corresponding novel trishomocubanones, the methyl and phenyl derivatives of **7** afforded products attributable to intramolecular hydrogen abstraction by the β-carbon of the α,β-unsaturated ketone along with the photocyclization products.

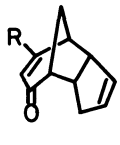
Because of the efficient construction of strained polycyclic molecules and the storage of solar energy, intramolecular photochemical [2+2] cyclizations of bridged dienes or dienones have attracted considerable attention in recent years. In particular, the conversion of dicyclopentadienone (**I**) to bishomocubanone is the best known example of such a reaction.[2] However, there have been no systematic studies on the photochemistry of the homologous dienones such as **II** or **III**, whose structural feature is very unique from the point of view that they have an allylic system facing to the conjugated enone moiety in the rigid molecule. These compounds are expected to undergo not only [2+2] photocyclization to give novel trishomocubane frameworks but also competitive intramolecular allylic hydrogen abstraction by the excited enones. Only a few examples are known for the photochemical reactions in which intramolecular hydrogen abstraction occurs competitively along with [2+2] photocyclization.[3,4]



I



II



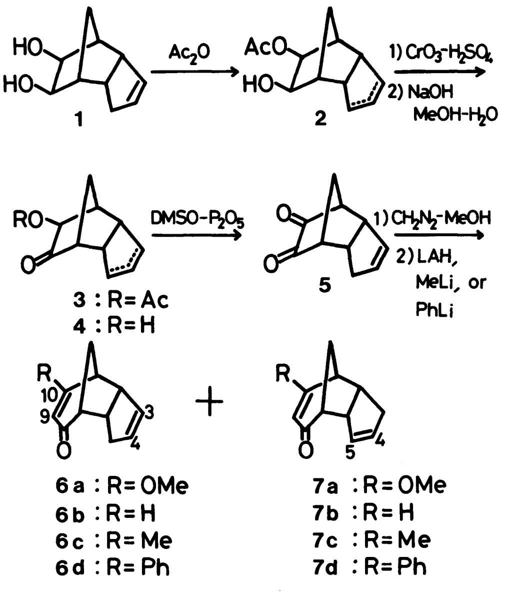
III

It seems to us of interest to synthesize the derivatives of **III** (**6a**—**d**) variously substituted at the β-carbon of the α,β-unsaturated enone and their isomers **7a**—**d** and to study their photochemical behavior. Details of such a study are reported herewith.

Results and Discussion

Syntheses of 10-Substituted Tricyclo[5.3.1.0^{2,6}]undecadienones. Scheme 1 shows the outline of the syntheses for **6a**—**d** and **7a**—**d**. The key compounds **6a** and **7a** were first synthesized starting from the diol **1**, which had been prepared by phase-transfer-assisted permanganate oxidation of *endo*-dicyclopentadiene in dichloromethane followed by treatment with an aqueous base.[5] Since it was difficult to oxidize **1** directly into the α-diketone **5**, the conversion was accomplished in the following manner. The diol (**1**) was partially acetylated with acetic anhydride at room temperature to give an isomeric mixture of the monoacetates **2**. Chromium trioxide oxidation of **2** followed by alkaline hydrolysis of the resulting keto acetates **3** afforded the α-ketol **4** as an isomeric mixture in 60% overall yield from **1**. The conversion of **4** into **5** with conventional oxidizing agents ($FeCl_3$–HCl, $Cu(OAc)_2$–AcOH, and $CuSO_4$–pyridine) failed. However, treatment of **4** with DMSO at 80—90 °C in the presence of P_2O_5[6] afforded **5** as a single product in 56% yield. The structure of **5** was supported by the spectral characteristics [IR 1770 and 1750 cm^{-1}; UV 475 nm (ε 24)], which are quite similar to those reported for camphorquinone.[7]

Treatment of **5** with diazomethane in diethyl ether in the presence of a small amount of methanol[8] gave an isomeric mixture of **6a** and **7a** in a 6 : 4 ratio via ring expansion and subsequent methylation of the resulting β-diketone. The mixture was separated by



Scheme 1.

preparative GLC or column chromatography on silica gel-$AgNO_3$. The IR (1640 and 1600 cm^{-1} for both **6a** and **7a**) and UV spectra [254 nm (ε 9300) for **6a**; 254 nm (ε 12900) for **7a**] exhibited the characteristic absorptions of α,β-unsaturated β-methoxycyclohexenone.

The assignments of the double-bond position in the cyclopentene rings of **6a** and **7a** were established by NMR studies using $Eu(dpm)_3$ as the shift reagent. The induced shifts determined for the olefinic proton signals are summarized in Table 1. Since the extremely large shift ($\Delta\delta$=5.56 ppm) observed for an olefinic proton of **7a** could be attributed to proximity of this hydrogen to the carbonyl group, **7a** were assigned to the structure having the double bond at C_4–C_5, and hence **6a** to the one having the double bond at C_3–C_4. This was further supported by the structures of the photoproducts of these compounds (vide infra).

The compound **6a** was then converted to **7b** (R=H), **7c** (R=Me), and **7d** (R=Ph) by reactions with LAH, MeLi, and PhLi, respectively, followed by acid treatment. In a similar fashion, **7a** was converted to **6b** (R=H), **6c** (R=Me), and **6d** (R=Ph). The structures of all the new compounds were evidenced by spectroscopic data (see Experimental), and the assignments of the double bond position were also compatible with the results of photolysis as described below.

Photolyses of the Tricyclo[5.3.1.0^{2,6}]undecadienones (6a—d and 7a—d). Irradiation of a benzene solution of **6a** in a Pyrex tube gave the [2+2] photocycloaddition product **8a** exclusively. The structure of the product was supported by the IR absorption at 1700 cm^{-1}, which indicated the presence of a six-membered cyclic ketone as expected from the structure of **6a** (but not **7a**), and also by the ^1H NMR spectrum, which was devoid of signals attributable to olefinic protons downfield from the methoxyl signal at δ 3.20.

Table 1. Induced Shifts of the Vinyl Proton Signals by $Eu(dpm)_3$

Compound	Hydrogen	$\Delta\delta^{a)}$ / ppm
6a	C_3-H	1.52
	C_4-H	1.52
7a	C_4-H	2.45
	C_5-H	5.56

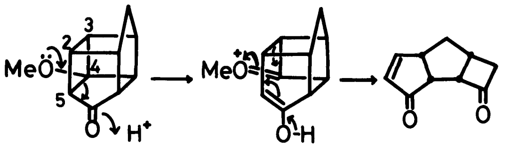
a) Changes in chemical shift at the molar ratio $Eu(dpm)_3$/substrate=1 extrapolated from the data observed at the ratio 0—0.18.

Treatment of **8a** with an acid in methanol gave **10**, a novel tetracyclic diketone, whose structure was deduced from the IR bands at 1765 (cyclobutanone) and 1700 cm^{-1} (cyclohexanone), and from the ^1H NMR spectrum (devoid of methoxyl signals).

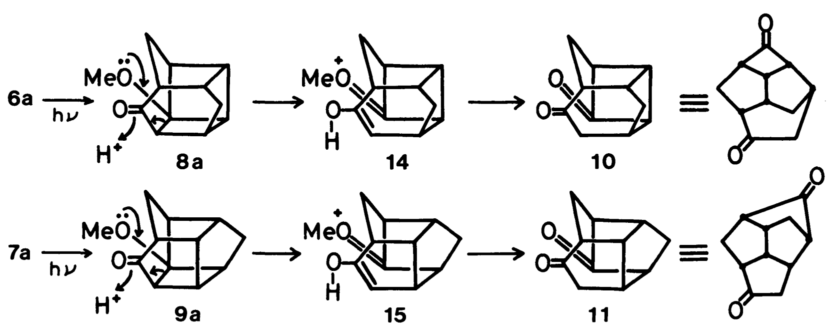
In a similar fashion, irradiation of **7a** gave an unstable cylization product **9a**, which was more easily transformed into the tetracyclic diketone **11** upon treatment with an acid, or even on standing in a refrigerator overnight, possively due to acidic impurities on the glass wall or in the solvent. The structure of **11** was also deduced from the spectroscopic data [IR absorption at 1735 cm^{-1} (cyclopentanone) and NMR spectrum devoid of methoxyl signal].

The formation of **10** and **11** can be rationalized by the retro-aldol type β-scission of the photoproducts (de Mayo reaction)[9] induced by protonation of the carbonyl groups and subsequent hydrolysis of the oxonium ions (**14** and **15**) as depicted in Scheme 2.

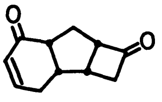
Recently, Zwanenburg, and co-workers[10] have reported a similar acid-catalyzed ring opening of methoxy-substituted bishomocubanone **16**. In this case, however, the initial scission of the C_4–C_5 bond is followed by subsequent C_2–C_3 bond cleavage, thus giving the tricyclic enedione **18**. The absence of signals due to olefinic protons in the ^1H NMR spectra of **10** and **11** can exclude the analogous enedione structures (**19** and **20**) for the ring opening products from **8a** and **9a**.



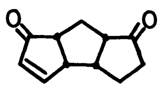
16 **17** **18**



Scheme 2.



19

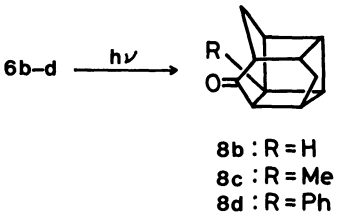


20

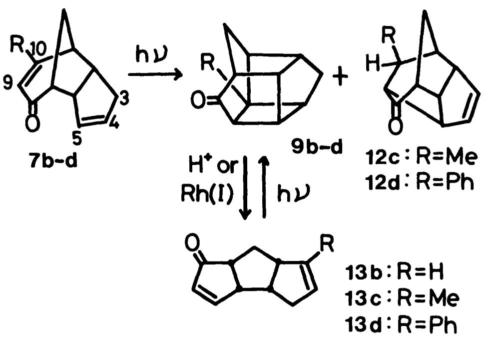
Irradiation of **6b**—**d** in benzene all resulted in the exclusive formation of trishomocubanones **8b**—**d** via [2+2] photocycloaddition (Scheme 3). The structures of the products were assigned by the IR absorptions (**8b**: 1695 $\mathrm{cm^{-1}}$, **8c**: 1685 $\mathrm{cm^{-1}}$, and **8d**: 1700 $\mathrm{cm^{-1}}$) which are compatible with cyclohexanones in polycyclic rigid systems[11] and by the ^{13}C NMR spectra which displayed no resonances for sp^2-hybridized carbon other than those assigned to the carbonyl carbon and the aromatic ring. Further evidence was given by the mass spectra which are almost superimposable on those of the corresponding starting dienones.

Irradiation of **7b** gave **9b** exclusively, whereas irradiation of **7c** and **7d** produced not only the photocyclization products **9c** and **9d**, but also additional photoproducts **12c**[12] and **12d**, respectively. The product ratios estimated by ^{1}H NMR were 5 : 1 for **9c**/**12c**, and 4 : 1 for **9d**/**12d**. Since any attempts to separate the products by chromatography failed in both cases, **9c** and **9d** were converted to the tricyclic dienones **13c** and **13d** by treatment with acids,[13] and then regenerated by irradiation after the chromatographic separation from unchanged **12c** and **12d**, respectively (Scheme 4).

Again, the structures of **9b**—**d** were supported by the IR spectra (**9b**: 1720 $\mathrm{cm^{-1}}$, **9c**: 1710 $\mathrm{cm^{-1}}$, and **9d**: 1725 $\mathrm{cm^{-1}}$), the ^{1}H NMR spectra (devoid of all low-field signals), and the ^{13}C NMR spectra (no resonances for sp^2-hybridized carbon other than those assigned to the carbonyl carbon and the aromatic ring). In addition, the mass-fragmentation patterns of this series of compounds (**9b**—**d**) were found to be quite similar to those of the dienones **13b**—**d**, respectively. The latter compounds have been obtained by acid or Rh(I)-catalyzed cycloreversion of **9b**—**d** and shown to reproduce the trishomocubanones (**9b**—**d**) upon irradiation (Scheme 4).[13,14] Recently, Mehta and coworkers have also established the similar interconversion between the pentacyclic diones **21** and the bis(enone)s **22**.[15]



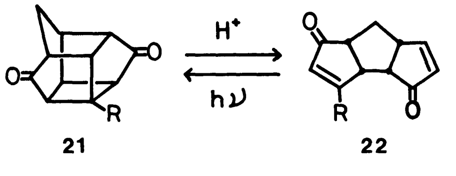
Scheme 3.

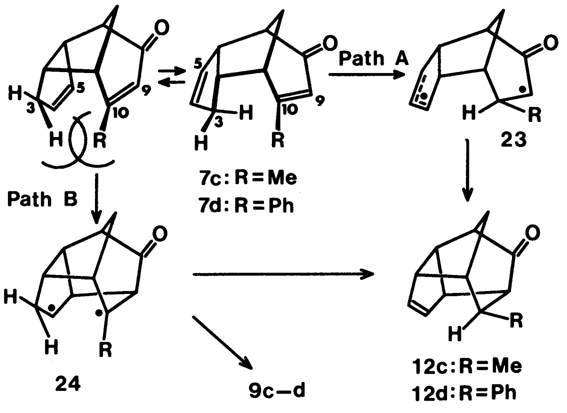


Scheme 4.

On the other hand, the ^{1}H NMR spectra of **12c** and **12d**, particularly the two olefinic proton signals at δ 5.79 (dd, J=6 and 3 Hz) and 6.10 (dd, J=6 and 3 Hz) for **12c**, and at δ 5.90 (dd, J=6 and 2.5 Hz) and 6.33 (dd, J=6 and 2.5 Hz) for **12d**, indicated that the double bond in the cyclopentene ring is retained in these compounds. This observation, coupled with the empirical formulae, $C_{12}H_{14}O$ for **12c** and $C_{17}H_{16}O$ for **12d**, determined by high-resolution mass spectra and elemental analysis suggested that these products have tetracyclic structures which are expected by intramolecular hydrogen abstraction. This was supported by the off-resonance ^{1}H decoupled ^{13}C NMR spectra. Namely, of the eleven skeletal carbons in each compound, one was accounted for by a signal for a carbonyl carbon [δ=219.2 (s) for **12c** and δ=218.5 (s) for **12d**], two were by signals for olefinic carbons [δ=133.6 (d) and 129.0 (d) for **12c**, and δ=134.8 (d) and 128.9 (d) for **12d**], seven were by signals for methine carbons [δ=54.5, 53.2, 52.7, 46.9, 45.8, 38.9, and 35.9 (all d) for **12c**, and δ=54.3, 52.9, 48.8, 46.5, 46.2, 45.8, and 40.6 (all d) for **12d**], and the remaining one was by a signal for a methylene carbon [δ=43.5 (t) for **12c**, and δ=42.4 (t) for **12d**]. These data, coupled with the appearance of the methyl signal as a doublet at δ 0.95 in ^{1}H NMR of **12c**, indicated that the hydrogen abstraction occurred at the β-carbon of the conjugated enone. Furthermore, of all the possible structures expected by hydrogen abstraction, only those depicted as **12c** and **12d** satisfied the IR spectra (1735 $\mathrm{cm^{-1}}$ for both **12c** and **12d**) which indicated the presence of the cyclopentanone rings.

Although a fair number of examples of the photoreactions which involve intramolecular allylic or benzylic hydrogen abstraction by the β-carbon of a conjugated enone have been reported,[16] a few examples of the reactions in which hydrogen abstrac-



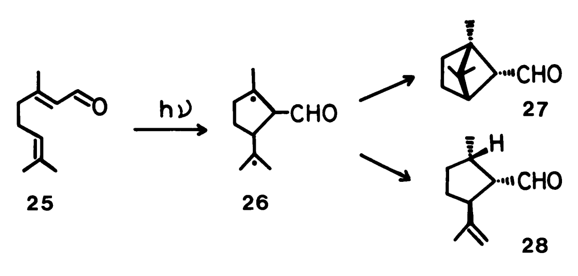


Scheme 5.

tion by the β-carbon occured along with intramolecular [2+2] photocyclization are known mainly with citral and related compounds.[4a)] The mechanistic possibilities (which cannot presently be distinguished) include the following.

Initial abstraction of the C_3-hydrogen atom by the β-carbon of a triplet enone (possively common to [2+2] cyclization) gives biradical **23** (path A in Scheme 5), which in turn collapses to **12**. Dreiding model examination of **7c—d** indicated that the β-carbon-to-C_3-hydrogen distance is 1.9—2.5 Å, which is within the limit for the sum of the van der Waals radii of 2.90 Å suggested for hydrogen abstraction by carbon.[17)] Furthermore, this inspection of the model disclosed that the substitution at C_{10} causes changes of the conformation so that the β-carbon-to-hydrogen distance becomes shorter and the hydrogen atom to be transferred becomes axial owing to the steric repulsion between the substituent and C_3-hydrogen. In this conformation, on the contrary, the spatial relationship of the two carbon–carbon double bonds comes to be unfavorable for the [2+2] cycloaddition reaction.

An alternative mechanism involves the initial bond formation between C_5 and C_9 to give the biradical **24** which may be a common intermediate for both **9c—d** and **12c—d** (path B in Scheme 5). A similar mechanism has been proposed for the photoreaction of citral (**25**) in which the biradical intermediate **26** derived from a triplet precursor led to both the [2+2] photocyclization product **27** and the hydrogen abstraction product **28**.[4a)] In addition, a same mechanism has been also proposed for the intermolecular photoreaction between 2-cyclohexenone and 2-methylpropene on the basis of the formation of 2-(2-methylallyl)cyclohexanone together with the corresponding cycloaddition product.[18)]



Although we prefer path A because this provides the explanation for the production of the hydrogen transfer products from the reaction of **7c** and **7d**, the present results do not define the detailed mechanism of the photoreaction.

Experimental

General. Melting points are uncorrected. IR spectra (in $CHCl_3$, unless otherwise noted) were recorded on JASCO A-102 and A-3 spectrometers. UV spectra were obtained on Hitachi 200-10 and JASCO UVIDEC-505 spectrometers. ^1H NMR spectra (in $CDCl_3$, unless otherwise noted) were determined on JEOL JNM-PMX 60 and Hitachi R-600 spectrometers with tetramethylsilane as the internal standard. ^{13}C NMR spectra (in $CDCl_3$) were obtained with a JEOL JNM-GX 270 spectrometer. GLC was performed on a Hitachi 063 gas chromatograph using PEG 20 M, DEGS, or Silicone SE-30. Mass spectra were taken on a Hitachi M-60 mass spectrometer at an ionization potential of 70 eV. High-resolution mass measurements were carried out on JEOL JMS-D-300 and Hitachi RMU-7MG mass spectrometers. Photochemical reactions were carried out in Pyrex tubes using 300 and 500 W high pressure mercury lamps, with running water cooling under a nitrogen atmosphere.

Preparation of Monoacetate 2. A solution of 3.05 g (18.3 mmol) of **1**[5)] in 50 cm^3 of freshly distilled Ac_2O was stirred at 30 °C for 19 h. The mixture was then poured into water (170 cm^3), stirred at room temperature for 2.5 h, and extracted with four 40 cm^3 portions of $CHCl_3$. The extracts were combined, washed with saturated aqueous $NaHCO_3$ and saturated brine, and dried ($MgSO_4$). Removal of the solvent under reduced pressure gave an oily residue which was purified on a silica-gel column (benzene–Et_2O) to afford pure **2** (3.12 g, 85%) as colorless crystals: Mp 68—70 °C. ^1H NMR (CCl_4) δ=2.00 (3H, s), 3.79 (1H, br. t, J=4 Hz), 4.50 (1H, t, J=6 Hz), and 5.62 (2H, br. s). IR 3600, 1720, and 1090 cm^{-1}. Found: C, 69.23; H, 7.67%. Calcd for $C_{12}H_{16}O$: C, 69.21; H, 7.74%.

Jones' Oxidation of 2 to Keto Acetate 3. To a well stirred solution of **2** (3.01 g, 14.5 mmol) in acetone (60 cm^3) was added Jones' reagent (12 cm^3) dropwise over a period of 1.5 h at 0 °C. After continued stirring for 30 min, the mixture was treated with 25% aqueous $NaHSO_3$ (20 cm^3), and concentrated to one-third of its original volume. The residue was poured into water, and extracted with $CHCl_3$ (60 cm^3×5). The combined extracts were washed with saturated aqueous $NaHCO_3$ and saturated brine, and dried over $MgSO_4$. Evaporation of the solvent in vacuo gave **3** (2.32 g, 78%) as pale yellow crystals. An analytical sample was prepared by recrystallization from Et_2O-pet. ether: Mp 62—64 °C. ^1H NMR (CCl_4) δ=2.00 (3H, s), 4.59 (1H, dd, J=14 and 3 Hz), and 5.67 (2H, m). IR 1755 and 1735 cm^{-1}. Found: C, 69.29; H, 6.84%. Calcd for $C_{12}H_{14}O_3$: C, 69.05; H, 6.94%.

Hydrolysis of 3 to α-Ketol 4. To a stirred solution of **3** (2.20 g, 10.7 mmol) in methanol (30 cm^3) was added a methanolic solution (10 cm^3) of NaOH (0.6 g, 15.0 mmol) dropwise over a period of 10 min at room temperature under a nitrogen atmosphere, and stirring was continued for 5 min. After evaporation of most part of the solvent, the residue was poured into water, and extracted with $CHCl_3$ (40 $cm^3 \times 5$). The extracts were washed with saturated brine, dried over $MgSO_4$, and evaporated in vacuo to give **4** (1.59 g, 91%) as pale yellow crystals. An analytical sample was prepared by recrystallization from Et_2O-pet. ether: Mp 64—69 °C. ^1H NMR (CCl_4) $\delta=3.30$ (1H, m), 3.54 (1H, m), and 5.60 (2H, br. s). IR 3600, 1750, and 1055 cm^{-1}. Found: C, 72.54; H, 7.80%. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37%.

DMSO Oxidation of 4 to α-Diketone (5). To a solution of **4** (6.18 g, 37.6 mmol) in dimethyl sulfoxide (110 cm^3) was added a solution of phosphorus pentoxide (16 g, 113 mmol) in DMSO (60 cm^3) at 90 °C over a period of 5 min. After standing for 30 min at 90 °C, the mixture was cooled, poured into water, and extracted with $CHCl_3$ (100 $cm^3 \times 5$). The extracts were washed with water, saturated aqueous $NaHCO_3$, and saturated brine and dried over $MgSO_4$. After removal of the solvent at reduced pressure, the residue was purified on a silica-gel column (benzene–Et_2O) to afford 3.42 g (56%) of **5** as yellow crystals. An analytical sample was prepared by recrystallization from Et_2O-pet. ether: Mp 58—60 °C. ^1H NMR $\delta=1.85$—3.85 (8H, m) and 5.53 (2H, br s). IR 1770 and 1750 cm^{-1}. UV (EtOH) 263 (ε 141) and 475 nm (ε 24). MS m/z 162 (M^+). Found: C, 73.17; H, 6.05%. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21%.

Preparation of 10-Methoxytricyclo[5.3.1.0^{2,6}]undeca-3,9-dien-8-one (6a) and 10-Methoxytricyclo[5.3.1.0^{2,6}]undeca-4,9-dien-8-one (7a) from 5. To a stirred solution of **5** (1.91 g, 11.8 mmol) in Et_2O (10 cm^3) were added an ethereal solution (100 cm^3) of diazomethane and MeOH (5 cm^3) in small portions at 0 °C, and the mixture was stirred overnight at room temperature. After evaporation of the solvent, separation of the residual oil (1.97 g) by preparative GLC (20% PEG 20 M on Chromosorb W-AW-DMCS, 230 °C) gave **6a** (0.89 g, 40%) as colorless crystals and **7a** (0.54 g, 24%) as a colorless oil. **6a**: Mp 67.5—69 °C. ^1H NMR $\delta=1.50$—2.35 (4H, m), 2.50—3.50 (4H, m), 3.53 (3H, s), 4.93 (1H, s), and 5.50 (2H, m). IR 1640 and 1600 cm^{-1}. UV (EtOH) 254 nm (ε 9300). MS m/z (rel intensity) 190 (M^+, 100), 175 (4), 125 (89), 124 (98), 109 (29), 106 (15), 96 (9), 92 (10), 91 (9). Found: C, 75.73; H, 7.26%; m/z 190.0983. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%; M, 190.0993. **7a**: ^1H NMR $\delta=1.50$—2.35 (4H, m), 2.50—3.50 (4H, m), 3.64 (3H, s), 4.91 (1H, s), and 5.48 (2H, s, $W_{1/2}=4$ Hz). IR 1640 and 1600 cm^{-1}. UV (EtOH) 254 nm (ε 12900). MS m/z (rel intensity) 190 (M^+, 100), 175 (3), 162 (10), 147 (20), 130 (11), 129 (11), 125 (61), 124 (100), 109 (60), 106 (91), 98 (21). Found: C, 75.20; H, 7.67%; m/z 190.0997. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%; M, 190.0993.

Preparation of Tricyclo[5.3.1.0^{2,6}]undeca-3,9-dien-8-one (6b) from 7a. To a refluxing mixture of $LiAlH_4$ (108 mg, 2.84 mmol) and dry Et_2O (20 cm^3) was added an anhydrous ethereal solution (5 cm^3) of **7a** (120 mg, 0.64 mmol). After refluxing for 2 h the mixture was cooled, treated with AcOEt (4 cm^3), and stirred with 25% H_2SO_4 (25 cm^3) at room temperature for 18 h. The organic solvent was evaporated in vacuo, and the aqueous solution was extracted with CH_2Cl_2 (15 $cm^3 \times 4$). The extracts were washed with saturated aqueous $NaHCO_3$ and saturated brine, dried over $MgSO_4$, and evaporated in vacuo. Purification of the residue by silica-gel chromatography (benzene–Et_2O) gave pure **6b** (55 mg, 55%); Mp 49—53 °C. ^1H NMR $\delta=1.54$—2.45 (4H, m), 2.65—3.30 (3H, m), 3.35—3.90 (1H, m), 5.56 (2H, br s, $W_{1/2}=6$ Hz), 5.90 (1H, d, $J=10$ Hz), and 6.93 (1H, dd, $J=10$ and 2 Hz). IR 1665 cm^{-1}. UV (EtOH) 230 nm (ε 4860). MS m/z (rel intensity) 160 (M^+, 26), 132 (5), 95 (100), 94 (30), 91 (13), 77 (25), 66 (38), 65 (13). Found: C, 81.99; H, 7.65%; m/z 160.0875. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%; M, 160.0888.

Preparation of Tricyclo[5.3.1.0^{2,6}]undeca-4,9-dien-8-one (7b) from 6a. To a suspension of lithium aluminum hydride (120 mg, 3.1 mmol) in dry Et_2O (45 cm^3) was added a solution of **6a** (121 mg, 0.64 mmol) in dry Et_2O (5 cm^3) under reflux and the mixture was heated for 1.5 h. Working up and purification similar to those employed for the synthesis of **6b** gave pure **7b** (52 mg, 51%) as colorless crystals: Mp 40—45 °C. ^1H NMR $\delta=1.50$—2.46 (4H, m), 2.53—3.25 (3H, m), 3.35—3.80 (1H, m), 5.55 (2H, s), 5.83 (1H, dd, $J=10$ and 2 Hz), and 7.10 (1H, br t, $J=8$ Hz). IR 1665 cm^{-1}. UV (EtOH) 236 nm (ε 5800). MS m/z (rel intensity) 160 (M^+, 41), 132 (53), 131 (20), 117 (86), 104 (27), 95 (37), 94 (18), 91 (57), 79 (32), 78 (61), 77 (45), 67 (29), 66 (100), 65 (36). Found: C, 82.16; H, 7.60%; m/z 160.0957. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%; M, 160.0888.

Preparation of 10-Methyltricyclo[5.3.1.0^{2,6}]undeca-3,9-dien-8-one (6c) from 7a. To a stirred solution of **7a** (118 mg, 0.62 mmol) in dry Et_2O (20 cm^3) at room temperature under nitrogen atmosphere was added a solution of methyllithium in Et_2O (1.85 mol dm^{-3}, 2.7 cm^3) over a period of 45 min. The reaction mixture was refluxed for 2 h, cooled to 0 °C, and treated with H_2SO_4 (3 mol dm^{-3}, 15 cm^3) for 50 min with vigorous stirring. Most of the organic solvent was evaporated, and the aqueous solution was extracted with $CHCl_3$ (30 $cm^3 \times 3$). The extracts were washed with saturated aqueous $NaHCO_3$, 3% aqueous Na_2SO_3 (20 cm^3) and saturated brine, dried ($MgSO_4$), and evaporated. Bulb-to-bulb (Kugelrohr) distillation of the residue [123—124 °C (1333 Pa)] gave pure **6c** (75 mg, 69%): Mp 42—45 °C. ^1H NMR $\delta=1.70$—2.36 (4H, m), 1.83 (3H, s), 2.40—3.26 (3H, m), 3.40—3.83 (1H, m), 5.53 (2H, br s, $W_{1/2}=3$ Hz), and 5.66 (1H, br s, $W_{1/2}=5$ Hz). IR 1655 and 1620 cm^{-1}. UV (EtOH) 238 nm (ε 7950). MS m/z (rel intensity) 174 (M^+, 32), 159 (4), 109 (100), 108 (31), 91 (18), 79 (12), 77 (14), 66 (13), 65 (12). Found: C, 82.35; H,8.25%; m/z 174.1028. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%; M, 174.1045.

Preparation of 10-Methyltricyclo[5.3.1.0^{2,6}]undeca-4,9-dien-8-one (7c) from 6a. To a stirred solution of **6a** (121 mg, 0.64 mmol) in dry Et_2O (20 cm^3) was added an ethereal solution of methyllithium (1.85 mol dm^{-3}, 2 cm^3) under nitrogen atmosphere at room temperature over a period of 50 min. The reaction mixture was worked up and purified by a method similar to that employed for the synthesis of **6c** to give **7c** (73 mg, 66%) as a colorless oil: ^1H NMR $\delta=1.70$—2.43 (4H, m), 2.02 (3H, s), 2.60—3.30 (3H, m), 3.30—3.80 (1H, m), 5.55 (2H, br s, $W_{1/2}=2$ Hz), and 5.65 (1H, br s, $W_{1/2}=5$ Hz). IR 1655 and 1620 cm^{-1}. UV (EtOH) 237 nm (ε 7300). MS m/z (rel intensity) 174 (M^+, 68), 159 (4), 146 (50), 131 (100), 117 (27), 106 (40), 105 (27), 93 (33), 92 (96), 91 (51), 80 (48). Found: C, 82.52; H, 8.13%; m/z 174.1025. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%; M, 174.1045.

Preparation of 10-Phenyltricyclo[5.3.1.0^{2,6}]undeca-3,9-dien-8-one (6d) from 7a. To a stirred solution of **7a**

(275 mg, 1.45 mmol) in dry Et_2O (30 cm^3) was added an ethereal solution of phenyllithium (1.66 mol dm^{-3}, 5.5 cm^3) at 0 °C over a period of 40 min under nitrogen atmosphere. The reaction mixture was refluxed for 3 h, poured into ice-cold 25% H_2SO_4 (20 cm^3), and stirred for 1 h. Most of the organic solvent was evaporatd, and the aqueous solution was extracted with $CHCl_3$ (50 cm^3×3). The extracts were washed with saturated aqueous $NaHCO_3$ and saturated brine, dried ($MgSO_4$), and evaporated. The residue was chromatographed on silica-gel (benzene–Et_2O) to give **6d** (214 mg, 62%) as colorless crystals: Mp 98—100 °C. ^1H NMR δ=1.70—2.43 (4H, m), 2.83—3.33 (2H, m), 3.35—3.93 (2H, m), 5.43 (2H, m), 6.22 (1H, s), and 7.42 (5H, br s). IR 1655 and 1600 cm^{-1}. UV (EtOH) 222 (ε 7530) and 290 nm (ε 13800). MS *m/z* (rel intensity) 236 (M^+, 57), 171 (100), 170 (71), 153 (56), 152 (22), 142 (20), 141 (21), 128 (21), 115 (36), 77 (23). Found: C, 86.28; H, 6.90%; *m/z* 236.1263. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82%; M, 236.1202.

Preparation of 10-Phenyltricyclo[5.3.1.0^{2,6}]undeca-4,9-dien-8-one (7d). To a stirred solution of **6a** (406 mg, 2.13 mmol) in dry Et_2O (45 cm^3) was added an ethereal solution of phenyllithium (1.66 mol dm^{-3}, 6.5 cm^3) at 0 °C under nitrogen atmosphere over a period of 1 h, and refluxed for another 40 min. The reaction mixture was poured into ice-cold 25% H_2SO_4 (40 cm^3), stirred vigorously for 100 min, and then worked up and purified by a method similar to that employed for the synthesis of **6d** to give **7d** (368 mg, 73%) as pale yellow crystals: Mp 68—71 °C. ^1H NMR δ=1.80—2.50 (4H, m), 3.00—3.36 (2H, m), 3.40—3.90 (2H, m), 5.57 (2H, br s), 6.20 (1H, s), and 7.43 (5H, br s). IR 1655 and 1600 cm^{-1}. UV (EtOH) 222 (ε 9540) and 290 nm (ε 15800). MS *m/z* (rel intensity) 236 (M^+, 77), 208 (34), 194 (29), 171 (56), 170 (57), 167 (31), 166 (29), 155 (100), 154 (43), 153 (21), 142 (93), 141 (54), 129 (26), 128 (38), 117 (24), 115 (72), 106 (99). Found: C, 86.15; H, 6.85%; *m/z* 236.1179. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82%; M, 236.1202.

Photochemical Transformation of 6a into 7-Methoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecan-9-one (8a). A solution of **6a** (10 mg) in benzene (3 cm^3) was irradiated for 6 h. Evaporation of the solvent in vacuo gave **8a** (10 mg) as a colorless oil, which was analyzed without purification because of its instability: ^1H NMR δ=1.50—1.83 (2H, m), 1.85—2.16 (2H, m), 2.50—3.83 (7H, m), and 3.20 (3H, s). IR 1700 cm^{-1}.

Acid Treatment of 8a. To a solution of **8a** (33 mg) in methanol (3 cm^3) was added ten drops of hydrochloric acid (1 mol dm^{-3}) at 50 °C. The mixture was stirred for 1.5 h, poured into saturated aqueous $NaHCO_3$ (10 cm^3), and extracted with $CHCl_3$ (10 cm^3×3). The extracts were washed with saturated brine, dried ($MgSO_4$), and evaporated to give the diketone **10** (25 mg, 82%) as colorless crystals: Mp 154—156 °C. IR 1765 and 1700 cm^{-1}. MS *m/z* (rel intensity) 176 (M^+ 4), 148 (72), 133 (14), 110 (18), 106 (11), 105 (34), 83 (12), 82 (100), 80 (12), 79 (34), 78 (29). Found: *m/z* 176.0838. Calcd for $C_{11}H_{12}O_2$: M, 176.0837.

Photochemical Transformation of 7a into 7-Methoxypentacyclo[5.4.0.0^{2,6}.0^{3,10}. 0^{4,8}]undecan-11-one (9a). Irradiation of a solution of **7a** (10 mg) in benzene (3 cm^3) for 2.5 h and evaporation of the solvent gave **9a** (10 mg) as an unstable colorless oil. ^1H NMR δ=1.50—2.50 (6H, m), 2.50—3.30 (5H, m), 3.50 (3H, s). IR 1730—1700 cm^{-1}.

Acid Treatment of 9a. To a solution of **9a** (12 mg) in methanol (2 cm^3) was added five drops of hydrochloric acid (1 mol dm^{-3}) at 75 °C. The mixture was stirred for 2 h, and worked up by a method similar to that described in the reaction of **8a** to give **11** (7 mg, 63%) as colorless crystals: Mp 118—120 °C. ^1H NMR δ=1.20—3.40 (12H, m). IR 1735 cm^{-1}. MS *m/z* (rel intensity) 176 (M^+, 100), 147 (65), 133 (16), 131 (25), 130 (12), 106 (13), 94 (22). Found: *m/z* 176.0868. Calcd for $C_{11}H_{12}O_2$: M, 176.0837.

Photochemical Transformation of 6b into Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecan-9-one (8b). Irradiation of a solution of **6b** (28 mg) in benzene (5 cm^3) for 2 h and purification of the product by column chromatography (benzene–Et_2O) gave **8b** (26 mg, 94 %) as a colorless oil. ^1H NMR δ=1.50—2.16 (4H, m) and 2.20—3.43 (8H, m). ^{13}C NMR δ=217.3 (s), 58.1 (d), 47.0 (d), 46.9 (d), 46.8 (d), 41.1 (d), 40.2 (d), 40.0 (d), 39.9 (t), 37.7 (d), and 34.6 (t). IR 1695 cm^{-1}. MS *m/z* (rel intensity) 160 (M^+, 31), 132 (15), 117 (27), 95 (100), 94 (35), 91 (27), 79 (15), 78 (21), and 77 (24). Found: C, 82.21; H, 7.60%; *m/z* 160.0876. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%; M, 160.0888.

Photochemical Transformation of 6c into 7-Methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecan-9-one (8d). Irradiation of a solution of **6c** (87 mg) in benzene (7 cm^3) for 3 h and purification of the product by chromatography (benzene–Et_2O) gave **8c** (70 mg, 81%) as a colorless oil. ^1H NMR δ=1.17 (3H,s), 1.47—2.10 (4H, m), and 2.15-3.30 (7H, m). ^{13}C NMR δ=217.1 (s), 57.1 (d), 54.0 (d), 46.4 (d), 46.1 (d), 45.1 (s), 44.0 (d), 43.7 (d), 38.0 (d), 38.0 (t), 34.8 (t), and 23.4 (q). IR 1685 cm^{-1}. MS *m/z* (rel intensity) 174 (M^+, 24), 159 (3), 146 (9), 131 (17), 109 (100), 108 (40), 93 (10), 92 (17), and 91 (29). Found: C, 82.45; H, 8.15%; *m/z* 174.0994. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%; M, 174.1045.

Photochemical Transformation of 6d into 7-Phenylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,8}]undecan-9-one (8d). Irradiation of a solution of **6d** (75 mg) in benzene (56 cm^3) for 10 h and purification of the product by chromatography (benzene–Et_2O) gave **8d** (30 mg, 40%): Mp 61—65.5 °C. ^1H NMR δ=1.60—1.90 (2H, m), 2.13 (2H, br s), 3.07 (5H, br s), 3.41 (2H, m), and 7.25 (5H, m). ^{13}C NMR δ=216.1 (s), 145.4 (s), 128.5 (d, 2C), 126.1 (d), 124.8 (d, 2C), 57.1 (d), 54.4 (d), 50.9 (s), 47.8 (d), 46.3 (d), 44.3 (d), 43.7 (d), 38.8 (t), 38.7 (d), and 34.82 (t). IR 1700 cm^{-1}. MS *m/z* (rel intensity) 236 (M^+, 25), 172 (11), 171 (100), 170 (61), 165 (15), 155 (16), 154 (16), 153 (40), 152 (20), 141 (21), 128 (16), 115 (34), and 102 (14). Found: C, 86.35; H, 6.85%; *m/z* 236.1206. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82%; M, 236.1202.

Photochemical Transformation of 7b into Pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecan-11-one (9b). Irradiation of a solution of **7b** (30 mg) in benzene (5 cm^3) for 2 h and purification by chromatography (benzene–Et_2O) gave **9b** (26 mg, 89%) as colorless crystals: Mp 116—118 °C. ^1H NMR δ=1.35—3.35 (12H, m). ^{13}C NMR δ=218.8 (s), 52.5 (d), 51.4 (d), 50.5 (d), 45.8 (d), 45.1 (d, 2C), 42.2 (t), 41.7 (d), 39.6 (d), and 35.6 (t). IR 1720 cm^{-1}. MS *m/z* (rel intensity) 160 (M^+, 43), 132 (56), 131 (25), 117 (100), 104 (30), 95 (28), 91 (60), 79 (64), 78 (81), 77 (38), 67 (23), and 66 (63). Found: C, 82.25; H, 7.62%; *m/z* 160.0909. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55%; M, 160.0888.

Photochemical Transformation of 7c into 7-Methylpentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]undecan-11-one (9c) and 10-Methyltetracyclo[5.3.1.0^{2,6}.0^{5,9}]undec-3-en-8-one (12c). Irradiation of a solution of **7c** (92 mg) in benzene (7 cm^3) for 2 h gave an inseparable mixture of **9c** and **12c** as a colorless solid. The ratio of **9c** to **12c** (5 : 1) was determined by the relative intensities of methyl proton signals in ^{1}H NMR. The mixture was treated with p-TsOH (50 mg) in benzene (10 cm^3) for 10 h at room temperature, washed with aqueous $NaHCO_3$ and brine, dried ($MgSO_4$). After evaporation of the solvent, the residue (79 mg) was chromatographed on silica gel to give **12c** (17 mg) and **13c**[13] (48 mg). **12c**: Mp 42—43 °C. ^{1}H NMR δ=0.95 (3H, d, J=7 Hz), 1.40—2.75 (7H, m), 2.80—3.40 (2H, m), 5.79 (1H, dd, J=6 and 3 Hz), and 6.10 (1H, dd, J=6 and 3 Hz). ^{13}C NMR δ=219.2 (s), 133.6 (d), 129.0 (d), 54.5 (d), 53.2 (d), 52.7 (d), 46.9 (d), 45.8 (d), 43.5 (t), 38.9 (d), 35.9 (d), and 16.5 (q). IR 1735 cm^{-1}. MS m/z (rel intensity) 174 (M$^+$, 56), 159 (14), 146 (54), 145 (31), 132 (26), 131 (82), 130 (24), 129 (31), 128 (29), 118 (37), 117 (69), 115 (51), 109 (72), 93 (76), 92 (87), and 91 (100). Found: C, 82.53; H, 8.12%; m/z 174.1017. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%; M, 174.1044.

Regeneration of 9c from 13c: Irradiation of a solution of **13c** (37 mg) in benzene (5 cm^3) for 3 h and purification of the product by chromatography (benzene–Et_2O) gave **9c** (34 mg, 94%) as colorless crystals: Mp 82—84 °C. ^{1}H NMR δ=1.10 (3H, s), 1.45—2.05 (4H, m), and 2.10—3.10 (7H, m). ^{13}C NMR δ=218.5 (s), 57.4 (d), 53.6 (s), 52.7 (d), 52.6 (d), 50.6 (d), 46.7 (d), 44.4 (d), 40.4 (d), 36.2 (d), 34.3 (t), and 23.1 (q). IR 1710 cm^{-1}. MS m/z (rel intensity) 174 (M$^+$, 69), 159 (6), 146 (56), 131 (100), 117 (31), 115 (21), 109 (80), 108 (35), 106 (34), 105 (30), 93 (77), 92 (99), and 91 (72). Found: C, 82.62; H, 8.11%; m/z 174.1017. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10%; M, 174.1045.

Photochemical Transformation of 7d into 7-Phenylpentacyclo$[5.4.0.0^{2,6}.0^{3,10}.0^{4,8}]$undecan-11-one (9d) and 10-Phenyltetracyclo$[5.3.1.0^{2,6}.0^{5,9}]$undec-3-en-8-one (12d). Irradiation of a solution of **7d** (64 mg) in benzene (6 cm^3) for 1.5 h gave a mixture of **9d** and **12d**. The ratio of **9d** to **12d** (4 : 1) was determined by the relative intensities of phenyl proton signals of **9d** and olefinic proton signals of **12d** in the ^{1}H NMR. The mixture was stirred with 3 drops of BF_3 etherate in benzene (10 cm^3) for 40 min at room temperature, washed with aqueos $NaHCO_3$ and brine, dried ($MgSO_4$), and the solvent was evaporated. Chromatography of the products (55.3 mg) gave **12d** (16 mg) and **13d**[13] (35.2 mg). **12d**: Mp 102—104 °C. ^{1}H NMR δ=1.9—3.5 (9H, m), 5.90 (1H, dd, J=6 and 2.5 Hz), 6.33 (1H, dd, J=6 and 2.5 Hz), and 7.28 (5H, m). ^{13}H NMR δ=218.2 (s), 142.7 (s), 134.8 (d), 128.9 (d), 128.4 (d, 2C), 127.6 (d, 2C), 126.1 (d), 54.3 (d), 52.9 (d), 48.8 (d), 46.5 (d), 46.2 (d), 45.8 (d), 42.4 (t), and 40.6 (d). IR 1735 cm^{-1}. MS m/z (rel intensity) 236 (M$^+$, 42), 208 (13), 171 (16), 170 (27), 166 (24), 155 (48), 154 (28), 143 (20), 142 (100), 141 (21), 129 (34), 128 (40), 117 (53), 116 (28), 115 (83), and 106 (66). Found: C, 86.26; H, 6.98%; m/z 236.1201. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82%; M, 236.1202.

Regeneration of 9d from 13d: Irradiation of a solution of **13d** (38 mg) in benzene (7 cm^3) for 90 min and purification of the product by column chromatography gave **9d** (31 mg, 82%) as colorless crystals: Mp 36.5—38 °C. ^{1}H NMR δ=1.50—2.40 (5H, m), 2.45—3.25 (6H, m), and 6.90—7.50 (5H, m). ^{13}C NMR δ=218.5 (s), 146.0 (s), 128.5 (d, 2C), 126.16 (d), 124.9 (d, 2C), 60.1 (s), 56.0 (d), 55.9 (d), 52.3 (d), 50.9 (d), 47.6 (d), 44.8 (d), 40.9 (t), 36.5 (d), and 35.7 (t). IR 1725 cm^{-1}. MS m/z (rel intensity) 236 (M$^+$, 40), 208 (16), 171 (35), 170 (29), 165 (15), 156 (14), 155 (100), 154 (26), 153 (16), 142 (41), 141 (29), and 115 (40). Found: C, 86.05; H, 7.01%; m/z 236.1221. Calcd for $C_{17}H_{16}O$: C, 86.41; H, 6.82%; M, 236.1202.

The authors wish to thank to Professors Hajime Katayama and Akira Kato of Niigata College of Pharmacy for the measurements of high-resolution mass spectra, and Professor Teruo Fujimoto and Mr. Takeo Kazama of Technological University of Nagaoka for the NMR measurements at 270 MHz. We also wish to express our thanks to Professor Koji Isogai and Mr. Jun-ichi Sakai of Niigata University for the measurements of mass spectra and their helpful discussions. This work was partially supported by Grant-in-Aids for Scientific Research (No. 56540295 and No. 58740240) from the Ministry of Education, Science and Culture.

References

1) A part of this study has been previously reported: T. Ogino and K. Awano, *Chem. Lett.*, **1982**, 891.

2) R. C. Cookson, R. R. Hill, and J. Hudec, *Chem. Ind. (London)*, **1958**, 100; R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Lett.*, **1960**, 29; G. Jones, II and B. R. Ramachandran, *J. Org. Chem.*, **41**, 798 (1976).

3) For examples of photoreactions which involve intramolecular hydrogen abstraction by the α-carbon of an α,β-unsaturated ketone system as well as intramolecular [2+2] cyclization, see T. W. Gibson and W. F. Erman, *J. Org. Chem.*, **37**, 1148 (1972); F. Nobs, U. Burger, and K. Schaffner, *Helv. Chim. Acta*, **60**, 1607 (1977); W. Oppolzer and T. G. C. Bird, *ibid.*, **62**, 1199 (1979); T. R. Hoye, S. J. Martin, and D. R. Peck, *J. Org. Chem.*, **47**, 331 (1982).

4) For examples of photoreactions which involve intramolecular hydrogen abstraction by the β-carbon of α,β-unsaturated ketone as well as intramolecular [2+2] cyclization, see a) R. C. Cookson, J. Hudec, S. A. Knight, and B. R. D. Whitear, *Tetrahedron*, **19**, 1995 (1963); G. Büchi and H. Wüest, *J. Am. Chem. Soc.*, **87**, 1589 (1965); F. Barany, S. Wolff, and W. C. Agosta, *ibid.*, **100**, 1946 (1978); **102**, 2378 (1980); b) M. Yoshioka, K. Ishii, and H. R. Wolf, *Helv. Chim. Acta*, **63**, 571 (1980); W. K. Appel, T. J. Greenhough, J. R. Scheffer, J. Trotter, and L. Walsh, *J. Am. Chem. Soc.*, **102**, 1160 (1980).

5) T. Ogino and K. Mochizuki, *Chem. Lett.*, **1979**, 443.

6) C. L. Stevens, *J. Org. Chem.*, **33**, 1586 (1968).

7) N. B. Haynes, D. Redmore, and C. J. Timmons, *J. Chem. Soc.*, **1963**, 2420.

8) von B. Eistert, D. Greiber, and I. Caspari, *Liebigs Ann. Chem.*, **654**, 64 (1962).

9) P. de Mayo and H. Takeshita, *Can. J. Chem.*, **41**, 440 (1963); B. D. Challand, H. Hikino, G. Kornis, G. Lange, and P. de Mayo, *J. Org. Chem.*, **34**, 794 (1964).

10) A. J. H. Klunder, G. J. A. Ariaans, and B. Zwanenburg, *Tetrahedron Lett.*, **25**, 5457 (1984).

11) K. Hirao, M. Taniguchi, O. Yonemitsu, J. L. Flippen, and B. Witkop, *J. Am. Chem. Soc.*, **101**, 408 (1979); K. Hirao, Y. Kajikawa, E. Abe, and O. Yonemitsu, *J. Chem. Soc., Perkin Trans. 1*, **1983**, 1791.

12) The compound **12c** was initially overlooked because it escaped detection even by GLC.[1]

13) T. Ogino, K. Awano, T. Ogihara, and K. Isogai, *Tetrahedron Lett.*, **24**, 2781 (1983).

14) T. Ogino, K. Awano, T. Ogihara, and K. Isogai, *Chem. Lett.*, **1984**, 2023.

15) G. Mehta and A. Srikrishna, *J. Chem. Soc., Chem. Commun.*, **1982**, 218.

16) For examples of the photoreactions which involve intramolecular allyic or benzylic hydrogen abstraction by the β-carbon of an α,β-unsaturated ketone system, see Y. Tamura, H. Ishibashi, and M. Ikeda, *J. Org. Chem.*, **41**, 1277 (1976); F. M. Schell and P. M. Cook, *ibid.*, **43**, 4420 (1978); S. Wolff, W. L. Schreiber, A. B. Smith, III, and W. C. Agosta, *J. Am. Chem. Soc.*, **94**, 7797 (1972); M. Tada, H. Saiki, H. Mizutani, and K. Miura, *Bull. Chem. Soc. Jpn.*, **51**, 343 (1978); M. Tada, T. Maeda, and H. Saiki, *ibid.*, **51**, 1516 (1978).

17) J. R. Scheffer and A. A. Dzakpasu, *J. Am. Chem. Soc.*, **100**, 2163 (1978).

18) E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Am. Chem. Soc.*, **86**, 5570 (1964).