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Singlet and Triplet Excited State Photochemistry of Tricyclo-[5.2.2.0^2,6^]undeca-3,10-dien-9-one Derivatives

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The photochemical behavior of tricyclo[5.2.2.$0^{2,6}$]undeca-3,10-dien-9-one ring system (**4**), which was prepared by Diels–Alder reaction of cyclohexadienone derivatives and cyclopentadiene, has been studied under triplet sensitization and direct irradiation. In the triplet state, this ring system undergoes the oxa-di-π-methane (ODPM) rearrangement, while the 1,3-acyl migration occurs from the singlet state. The triplet energy was estimated to be between 70 and 72 kcal/mol on the basis of sensitization by various sensitizers.

Keywords——Diels–Alder adduct; β-γ-unsaturated ketone; triplet energy; oxa-di-π-methane rearrangement; 1,3-acyl migration; cyclopropyl ketone; cyclobutanone

Photochemical reactions of Diels–Alder adducts are very useful for the synthesis of polycyclic cage compounds, and many examples have been reported.[2] However, even minor modifications and variations in structure of starting substrates and/or in reaction conditions sometimes bring about complicated results. For example, the reactivity of *endo*-dicyclopentadiene (**1a**),[3] *endo*-tricyclo[5.2.2.$0^{2,6}$]undeca-3,8-diene (**2**),[4] and *endo*-dicyclohexadiene (**3a**)[5] toward photochemical cycloaddition decreases in that order. On the other hand, oxo derivatives of these compounds show different reactivities. Thus, **3b**, a dioxo derivative of **3a**, gives exclusively an intramolecular cycloaddition product,[6] whereas **1b** gives various compounds being influenced by irradiation conditions.[7] Compound **1c** having only an $\alpha\beta$ unsaturated ketone again gives solely a cycloaddition product.[8]

In the present paper, we have examined the reactivity of another type of mono-oxo derivatives (**4**), which have a $\beta\gamma$-unsaturated ketone, not an $\alpha\beta$-unsaturated one. Considering the structure of **4**, we can expect many photochemical reactions,[9] that is, oxa-di-π-methane (ODPM) rearrangement, intra- and intermolecular cycloaddition, reduction, and hydrogen transfer *via* an excited triplet state, and 1,3-sigmatropic acyl shift and decarbonylation *via* an excited singlet state. But the factors which influence the competition among these photoreactions are not understood yet.

Diels-Alder adducts (**4**) used in this study were synthesized in good yield from cyclohexadienones and cyclopentadiene or *cis*-butene by refluxing their xylene solution.

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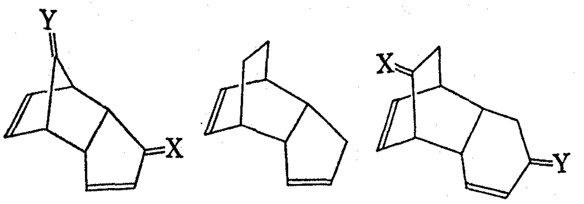
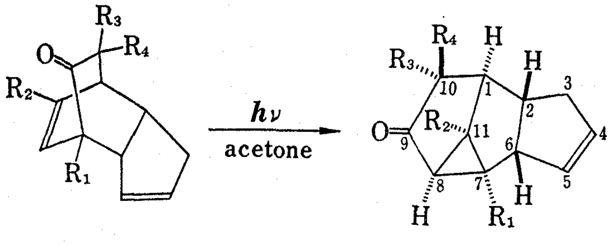


1a: $X=Y=H_2$
1b: $X=Y=O$
1c: $X=O, Y=H_2$

3a: $X=H_2$
3b: $X=O$

Chart 1



4 **5**

a: $R_1=R_2=H, R_3=Me, R_4=OH$
b: $R_1=R_2=R_3=Me, R_4=OH$
c: $R_1=R_3=R_4=Me, R_2=H$

Chart 2

Triplet Sensitized Reaction

A solution of the adduct (**4a**) in acetone was irradiated with a 100 W high pressure mercury lamp through a Pyrex filter for 6 hr. Because the product (**5a**) was unstable to further irradiation, the reaction was stopped when the decomposition of **5a** was observed by thin-layer chromatography (TLC). The reaction mixture was chromatographed over silica gel to give the recovered **4a** (29%) and the product (**5a**, 26%).

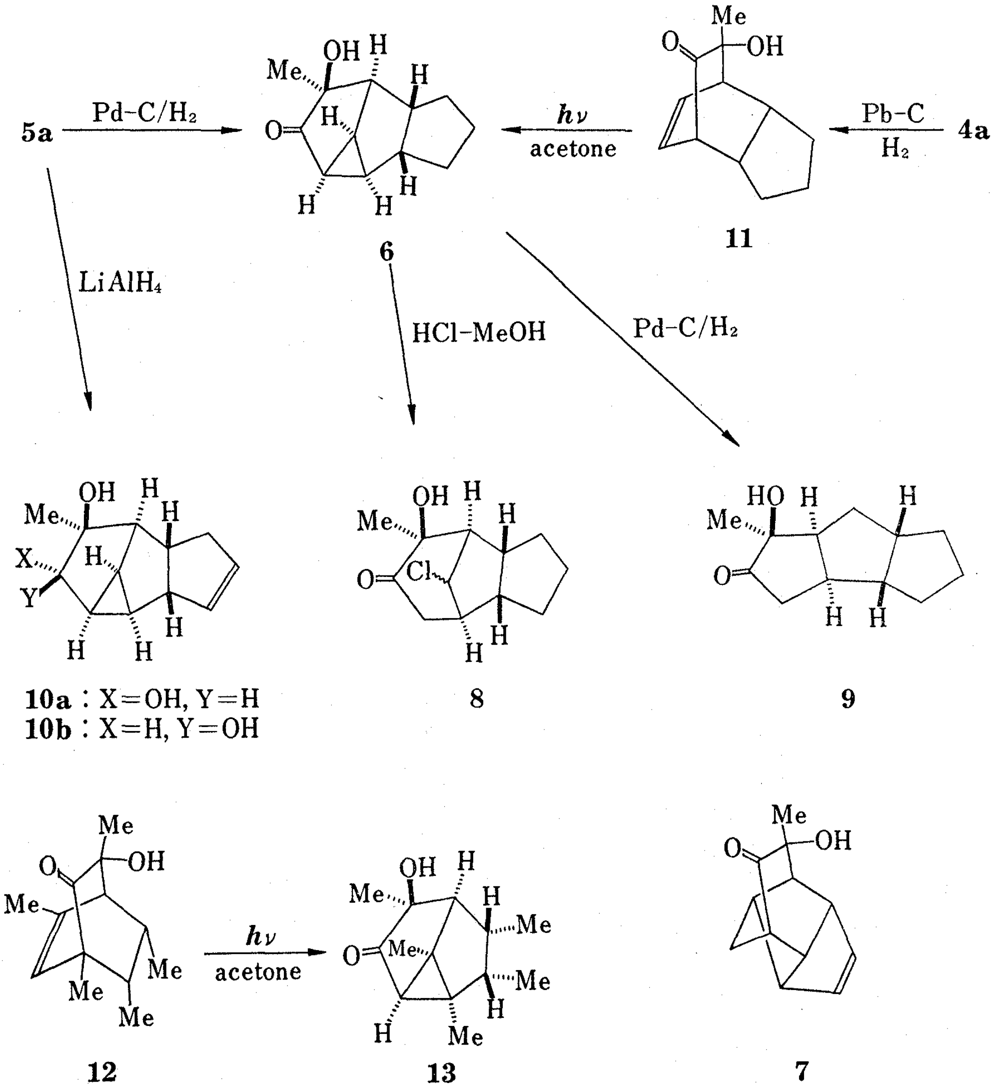


Chart 3

On the basis of elemental analysis, mass spectrum (MS), and molecular weight determination by the vapor pressure method, the composition of **5a** was determined as $C_{12}H_{14}O_2$ isomeric with the starting material (**4a**). In the nuclear magnetic resonance (NMR) spectrum, two vinyl protons appeared in the same position at 5.70 ppm indicating that **5a** still had a double bond, which was readily reduced to **6** by catalytic hydrogenation (5% Pd-C, 3 atm). These spectral data showed that the structure of the photoproduct was either **5a** formed by an ODPM rearrangement or **7** formed by an intramolecular abstraction of allylic hydrogen, though their distinction was not available even in the ^{13}C–NMR spectrum.

The following facts revealed that the ODPM rearrangement actually took place. First, the presence of a cyclopropane ring was proved as follows. On treatment of **6** with hydrogen chloride in methanol at room temperature, the addition of hydrogen chloride occurred selectively at the C_8–C_{11} bond to give a six-membered ketone (**8**), which was shown by its infrared (IR) spectrum (1710 cm^{-1}). Further hydrogenation (5% Pd-C, 5.6 atm) of **6** gave a tetrahydro derivative (**9**) having a five-membered ketone (IR: 1740 cm^{-1}). On treatment with deuteromethanol (MeOD) in the presence of sodium methoxide, **9** incorporated two deuteriums showing that the reductive opening of the cyclopropane ring in **6** occurred selectively at the C_7–C_8 bond. In the NMR spectra of diols, **10a** and **10b**, obtained from **5a** by lithium aluminum hydride reduction, signals of cyclopropane ring protons were observed at 1.4—1.6 and 1.0—1.4 ppm.10) Second, on irradiation in acetone, the dihydro compound (**11**) obtained by partial hydrogenation of **4a** also gave **6**. Because of the absence of a double bond at C_3, hydrogen abstraction leading to a **7**-type product must be an inefficient process.

Irradiation of analogous compounds, **4b**, **4c**, and **12** in acetone also led to the same type of products **5b**, **5c**, and **13** in 27, 19, and 25% yield, respectively. Accordingly, among many possible reactions occurring from the excited triplet state, the photochemistry of this ring system (**4**) is dominated by ODPM rearrangement.

Many studies on the photochemistry of $\beta\gamma$-unsaturated ketones have been reported.9) Recently, the triplet energies (E_T) of these ketones were summarized by Hancock and Grider11) as being generally less than 70 kcal/mol on the basis of phosphorescence spectroscopy, whereas more recently, Engel, *et al.* estimated that E_T lies between 74 and 78 kcal/mol by kinetic studies.12)

The photoreaction of **4a** was sensitized with aniline (E_T=76 kcal/mol), acetophenone (74), diphenylamine (72), and benzophenone (69), and not with triphenylamine (70), carbazole (70), and triphenylene (67). These data show that E_T of **4a** may be between 70 and 72 kcal/mol. However, benzophenone having E_T less than 70 kcal/mol clearly acted as a sensitizer. This contradiction may be resolved by considering the formation of an excited complex between **4a** and an aromatic ketone.12)

Singlet State Photochemistry

When an ethyl acetate solution of **4a** was irradiated with the 100 W lamp through a Pyrex filter, a new absorption at 1780 cm^{-1} in the IR spectrum of the reaction mixture gradually increased, indicating the formation of a four-membered ketone by a 1,3-acyl shift. The product, however, was too unstable to be isolated, so after irradiation, the reaction mixture was immediately hydrogenated over palladium-carbon to give a tetrahydro derivative (**14**), which still has a four-membered ketone (IR: 1765 cm^{-1}). Similarly, **4c** gave **15**, which could be isolated by silica gel chromatography, though **15** was also rather unstable and apt to

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10) The cyclopropane ring protons in **5a** and **6** are shifted to downfield owing to the deshielding effect of carbonyl groups.

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decompose during the chromatography. In its IR spectrum, **15** has a four-membered ketone (1775 cm^{-1}), and other spectral data support the assigned structure.

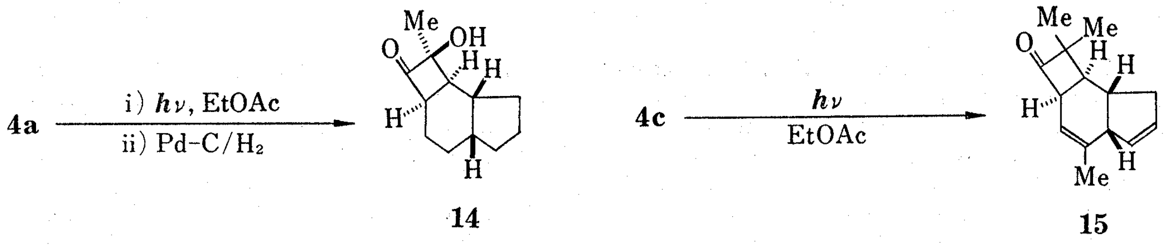

Chart 4

In conclusion, the tricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-9-one derivatives (**4**) behave in their photochemistry solely as a $\beta\gamma$-unsaturated ketone system, regardless of the cyclopentene ring, and exclusively occur the ODPM rearrangement from the triplet excited state and the 1,3-acyl migration from the singlet excited state.

Experimental

8-Hydroxy-8-methyltricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (4a)——A xylene solution (400 ml) of 2-methyl-*o*-quinolacetate (40 g) and cyclopentadiene (40 ml) was heated under reflux for 12 hr. After removal of the solvent, the residue was dissolved in MeOH (400 ml) and 10% NaOH (150 ml). The solution was allowed to stand at room temperature for 1 hr, and then acidified to pH 5 by the addition of HCl. After removal of the MeOH, the precipitated solid was collected by filtration, and chromatographed on silica gel using EtOAc–hexane as eluent to obtain, after recrystallization from EtOAc–hexane, 15.5 g (33.8%) of colorless prisms of **4a**, mp 124—126°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3400, 1715. UV $\lambda_{\max}^{\text{MeOH}}$ nm (ε): 306 (60). MS *m/e* (%): 190 (M$^+$, 4), 149 (26), 124 (22), 66 (100). NMR (CDCl$_3$) δ: 1.28 (3H, s), 5.36—5.50 (1H, m), 5.64—5.76 (1H, m), 6.04 (1H, dt, $J=7$, 1 Hz), 6.32 (1H, dt, $J=7$, 1 Hz). *Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.77; H, 7.44. Found: C, 75.76; H, 7.42.

8-Hydroxy-1,8,11-trimethyltricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (4b)——A xylene solution (40 ml) of 2,4,6-trimethyl-*o*-quinolacetate (5.0 g) and cyclopentadiene (5.0 g) was refluxed for 10 hr. Work-up as described above gave 4.7 g of crude crystals of **4b**, which was recrystallized from EtOAc–hexane to give 3.16 g (56%) of colorless prisms, mp 155—157°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3400, 1710. NMR (CDCl$_3$) δ: 1.07 (3H s), 1.23 (3H, s), 1.87 (3H, d, $J=2$ Hz), 5.26 (1H, broad s), 5.40—5.60 (1H, m), 5.67—5.88 (1H, m). MS *m/e* (%): 218 (M$^+$, 23), 152 (23), 110 (100), 66 (49). *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 73.82; H, 7.74. Found: C, 73.92; H, 7.81.

1,8,8-Trimethyltricyclo[5.2.2.0^{2,6}]undeca-3,10-dien-9-one (4c)——A xylene solution (180 ml) of 2,6,6-trimethylcyclohexadienone (4.9 g) and dicyclopentadiene (14 ml) was refluxed for 7.5 hr. Work-up as described above gave 6.8 g (93%) of **4c** as a colorless oil, bp 125—130° (bath temp)/13 Torr. IR $\nu_{\max}^{\text{neat}}$ cm^{-1}: 1710. NMR (CCl$_4$) δ: 1.02 (3H, s), 1.09 (3H, s), 1.16 (3H, s), 5.55 (1H, s), 5.58 (1H, s), 5.72 (1H, broad s), 6.18 (1H, m). MS *m/e* (%): 202 (M$^+$, 5), 137 (100), 136 (69), 131 (62), 117 (88), 93 (57), 91 (38), 66 (61). *Anal.* Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.88; H, 9.13.

Sensitized Irradiation of 4a in Acetone——An acetone solution (80 ml) of **4a** (969 mg) was irradiated with a 100 W high pressure mercury lamp (Eikosha PIH-100) through a Pyrex filter for 6 hr. After removal of the acetone, the residue was chromatographed over silica gel eluting with EtOAc–hexane to give 280 mg (29%) of the starting material (**4a**) and 250 mg (26%) of 10-hydroxy-10-methyltetracyclo[5.3.1.0^{2,6}.0^{8,11}]-undec-4-en-9-one (**5a**), which was recrystallized from EtOAc–hexane to give colorless prisms, mp 109—111°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3400, 1710. $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1}: 3530, 1726. ^{1}H-NMR (CDCl$_3$) δ: 1.35 (3H, s), 1.8—1.9 (2H, m), 2.1—2.4 (1H, m), 2.4—2.65 (3H, m), 2.7—3.1 (3H, m), 5.70 (2H, s). ^{13}C-NMR (CDCl$_3$) δ: 26.9 (q), 29.9 (d), 30.0 (d), 36.1 (d), 38.8 (t), 47.5 (d), 50.7 (d), 54.5 (d), 82.4 (s), 132.0 (d), 132.5 (d), 199.5 (s). MS *m/e* (%): 190 (M$^+$, 3), 149 (68), 119 (57), 91 (100). Molecular Weight (Vapor phase osmometric method): 183.9. *Anal.* Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.73; H, 7.43.

10-Hydroxy-10-methyltetracyclo[5.3.1.0^{2,6}.0^{8,11}]undecan-9-one (6)——A MeOH solution (80 ml) of **5a** (1.26 g) was hydrogenated over 5% Pd-C (200 mg) at 3 atm for 30 min. After filtration of the catalyst, the filtrate was evaporated to leave a solid, which was recrystallized from EtOAc–hexane to give 1.15 g (91%) of colorless prisms, mp 77.5—79°. IR $\nu_{\max}^{\text{Nujol}}$ cm^{-1}: 3355, 1710. NMR (CDCl$_3$) δ: 1.32 (3H, s). MS *m/e* (%): 192 (M$^+$, 63), 149 (44), 121 (81), 107 (100), 91 (61), 79 (79). *Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.92; H, 8.43.

11-Chloro-8-hydroxy-8-methyltricyclo$[5.3.1.0^{2,6}]$undecan-9-one (8)——Compound **6** (75 mg) was dissolved in HCl–MeOH (5 ml), and stirred for 20 min at room temperature. After removal of the solvent, the residue (89 mg, 100%, one spot on TLC) was recrystallized from EtOAc–hexane to give colorless prisms, mp 87—88°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3480, 1710. MS *m/e* (%): 202 (3), 200 (12), 165 (100), 147 (3), 121 (43), 107 (57). NMR ($CDCl_3$) δ: 1.42 (3H, s), 4.73 (1H, s). *Anal.* Calcd. for $C_{12}H_{17}ClO_2$: C, 63.02; H, 7.48; Cl, 15.23. Found: C, 62.97; H, 7.58; Cl, 15.50.

5-Hydroxy-5-methyltricyclo$[6.3.0.0^{2,6}]$undecan-4-one (9)——A MeOH solution of **6** (200 mg) was hydrogenated over 5% Pd-C (200 mg) at 5.6 atm for 7 hr. After removal of the catalyst and evaporation of the solvent, the residue was recrystallized from EtOAc–hexane to give 127 mg (63%) of colorless prisms, mp 90.5—92.5°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3450, 1740. NMR ($CDCl_3$) δ: 1.28 (3H, s). MS *m/e* (%): 194 (M^+, 6), 166 (12), 148 (100), 108 (26). *Anal.* Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.18; H, 9.33.

Deuteration of 9——A solution of **9** (10 mg) in MeOD (1 ml) containing of NaOMe (3 mg) was stirred at room temperature for 24 hr. After neutralization by blowing CO_2 and evaporation of the solvent, the residue was dissolved in EtOAc and washed with water. The EtOAc layer was dried, and evaporated to leave a colorless solid. MS *m/e*: 196 (M^+), 168, 150, 110.

Reduction of 5a with $LiAlH_4$——To stirred $LiAlH_4$ (40 mg) in THF (2 ml) at 5° **5a** (175 mg) in THF (5 ml) was added dropwise. After 30 min, a small amount of water was added, then the precipitated white solid was filtered off, and washed with EtOAc. The combined solution was evaporated, and chromatographed on silica gel eluting with EtOAc–hexane to give two fractions. The first fraction was 9β,10β-dihydroxy-10-methyltetracyclo$[5.3.1.0^{2,6}.0^{8,11}]$undec-4-ene (**10b**), mp 62—64°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3280. NMR ($CDCl_3$) δ: 1.30 (3H, s), 1.4—1.64 (2H, m), 1.88—2.10 (1H, m), 4.06 (1H, d, $J=6$ Hz), 5.61 (2H, s). MS *m/e* (%): 192 (M^+, 1), 174 (8), 156 (10), 149 (98), 131 (51), 117 (44), 105 (100), 91 (74). *Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.96; H, 8.36.

The second fraction was 62.8 mg (36%) of colorless prisms of 9α,10β-dihydroxy-10-methyltetracyclo$[5.3.1.0^{2,6}.0^{8,11}]$undec-4-ene (**10a**), mp 109—110°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3450, 3300. NMR ($CDCl_3$) δ: 1.10 (1H, t, $J=7$ Hz), 1.12 (1H, q, $J=8$ Hz), 1.31 (3H, s), 1.25—1.44 (1H, m), 1.8—2.2 (3H, m), 3.75 (1H, d, $J=4$ Hz), 5.62 (2H, s). MS *m/e* (%): 174 (7), 156 (100), 131 (62), 117 (53), 105 (60), 91 (85). *Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.93; H, 8.35.

11-Hydroxy-11-methyltricyclo$[5.2.2.0^{2,6}]$undec-8-en-10-one (11)——A MeOH solution (20 ml) of **4a** (190 mg) was hydrogenated over 5% Pd-C (12 mg) at 1.7 atm for 30 min. After removal of the catalyst, the solvent was evaporated to leave a solid, which was recrystallized repeatedly from EtOAc–hexane to give 38 mg (20%) of colorless prisms, mp 93.5—94°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3400, 1710. NMR ($CDCl_3$) δ: 1.28 (3H, s), 6.10 (1H, t, $J=6$ Hz), 6.40 (1H, t, $J=6$ Hz). MS *m/e* (%): 192 (M^+, 3), 164 (12), 121 (100), 91 (29). *Anal.* Calcd. for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.80; H, 8.56.

Sensitized Irradiation of 11 in Acetone——An acetone solution (10 ml) of **11** (44.5 mg) was irradiated for 5 hr and post-treated as described above to give 18 mg (40%) of **6**, which was recrystallized from EtOAc–hexane to give colorless prisms, mp 76.5—78.5°.

Sensitized Irradiation of 4b in Acetone——An acetone solution (80 ml) of **4b** (400 mg) was irradiated as described above for 6.5 hr to give 97 mg (24%) of the starting material (**4b**) and 83 mg (21%) of 10-hydroxy-7,10,11-trimethyltetracyclo$[5.3.1.0^{2,6}.0^{8,11}]$undec-4-en-9-one (**5b**) as a colorless solid. Recrystallization from EtOAc–hexane gave colorless prisms, mp 92—93.5°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3400, 1710. NMR ($CDCl_3$) δ: 1.09 (3H, s), 1.34 (3H, s), 1.41 (3H, s), 5.72 (2H, broad s). MS *m/e* (%): 218 (M^+, 11), 153 (48), 147 (56), 110 (100), 91 (50). *Anal.* Calcd. for $C_{14}H_{18}O_2$: C, 73.82; H, 7.74. Found: C, 74.08; H, 7.88.

Sensitized Irradiation of 4c in Acetone——An acetone solution (80 ml) of **4c** (450 mg) was irradiated as described above for 3 hr to give 269 mg (59%) of the starting material (**4c**) and 84 mg (19%) of 7,10,10-trimethyltetracyclo$[5.3.1.0^{2,6}.0^{8,11}]$undec-4-en-9-one (**5c**), bp 145—150° (bath temp.)/13 Torr. IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}: 1715. NMR (CCl_4) δ: 0.88 (3H, s), 1.08 (3H, s), 1.12 (3H, s), 1.66 (1H, d, $J=6$ Hz), 5.72 (2H, s). MS *m/e* (%): 202 (M^+, 38), 187 (33), 161 (32), 159 (46), 95 (100), 91 (50). *Anal.* Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.08; H, 8.96.

3-Hydroxy-1,3,5,7,8-pentamethylbicyclo[2.2.2]oct-5-en-2-one (12)——A benzene (50 ml) solution of 2,4,6-trimethyl-*o*-quinol (1 g) and 2-butene (8 g) in a sealed tube was heated at 145—150° for 21.5 hr. After removal of the solvent, the residue was chromatographed on silica gel eluting with EtOAc–hexane (1: 3) to give 514 mg (38%) of **12**. Recrystallization from aq. MeOH gave colorless needles, mp 95—96°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3420, 1710. NMR ($CDCl_3$) δ: 0.80 (3H, d, $J=7$ Hz), 0.86 (3H, d, $J=7$ Hz), 1.14 (3H, s), 1.24 (3H, s), 1.72—2.08 (1H, m), 1.92 (3H, broad s), 2.42 (1H, t, $J=2$ Hz), 2.56—2.90 (1H, m), 5.34 (1H, m). MS *m/e* (%): 208 (M^+, 5), 180 (17), 152 (11), 137 (100), 135 (48), 121 (24), 119 (15). *Anal.* Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.71; H, 9.60.

Sensitized Irradiation of 12 in Acetone——An acetone solution (40 ml) of **12** (200 mg) was irradiated as described above for 8 hr to give 73 mg (37%) of the starting material (**12**) and 49 mg (25%) of 4-hydroxy-1,4,6,7,8-pentamethyltricyclo$[3.2.1.0^{2,8}]$octan-3-one (**13**). Recrystallization from aq. MeOH gave colorless prisms, mp 111—112°. IR $\nu_{\max}^{\mathrm{Nujol}}$ cm^{-1}: 3370, 1710. NMR (CCl_4) δ: 0.86 (3H, d, $J=4$ Hz), 0.97 (3H, d, $J=4$ Hz), 1.15 (3H, s), 1.20 (3H, s), 1.43 (3H, s). MS *m/e* (%): 208 (M^+, 1), 190 (63), 175 (61), 147 (71), 137 (100), 95 (63), 91 (38). *Anal.* Calcd. for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.73; H, 9.71.

Direct Irradiation of 4a in EtOAc——An EtOAc solution (40 ml) of **4a** (400 mg) was irradiated with the 100 W high pressure lamp through a Pyrex filter for 2 hr, then the reaction mixture was hydrogenated over 5% Pd-C (100 mg) at 3 atm for 30 min. After removal of the catalyst and evaporation of the solvent, the residue was chromatographed on silica gel eluting with EtOAc–hexane to give 30 mg (7%) of 3-hydroxy-3-methyltricyclo[6.3.0.$0^{2,5}$]undecan-4-one (**14**) as a colorless oil. IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}: 3400, 1765. MS *m/e* (%): 194 (M^+, 13), 166 (54), 151 (35), 121 (100), 67 (81).

Direct Irradiation of 4c in EtOAc——An EtOAc solution (30 ml) of **4c** (200 mg) was irradiated for 1.5hr as the foregoing experiment. After evaporation of the solvent, the residue was chromatographed on silica gel eluting with EtOAc–hexane to give 18 mg (9%) of 3,3,7-trimethyltricyclo[6.3.0.$0^{2,5}$]undeca-6,9-dien-4-one (**15**) as a colorless oil. IR $\nu_{\text{max}}^{\text{neat}}$ cm^{-1}; 1775. NMR ($CDCl_3$) δ: 1.13 (6H, s), 1.73 (3H, broad s), 3.00 (1H, m), 3.70 (1H, m), 5.40 (1H, m), 5.76 (1H, m), 5.88 (1H, m). MS *m/e* (%): 202 (M^+, 1), 137 (26), 131 (38), 117 (100), 91 (46), 65 (19).