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Chemistry of 2-Methoxy-2,5-cyclohexadienone. IV.[1] Photochemistry of 2-Methoxy-4,4-diphenyl-2,5-cyclohexadienone and 4-Dichloromethyl-2-methoxy-4-methyl-2,5-cyclohexadienone[2]

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2-Methoxy-4,4-diphenyl-2,5-cyclohexadienone (Ib) was irradiated with a 100 W mercury lamp in methanol to give methyl 5-methoxy-6,6-diphenyl-2,5-hexadienoate (II) or its oxidized product, 9-(4-carbomethoxy-1-methoxy-2-butenylidene)-9*H*-fluorene (IV), and in benzene to give 6-methoxy-5,6-diphenyl-2,4-cyclohexadienone (VI) and 1-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (VII). 2-Methoxy-4,4-diphenyl-2-cyclohexenone (XIa) was irradiated in benzene or methanol to give 1-methoxy-5,6-diphenylbicyclo[3.1.0]hexan-2-one (XII) in good yield. Finally, 4-dichloromethyl-2-methoxy-4-methyl-2,5-cyclohexadienone (Ic) in methanol gave 6-dichloromethyl-2,2-dimethoxy-6-methylbicyclo[3.1.0]hexan-3-one (XIV) and 5-dichloromethyl-6,6-dimethoxy-5-methyl-2-cyclohexenone (XV).

Keywords——photochemistry; 2,5-cyclohexadienone; 2-methoxy-2,5-cyclohexadienone; 2-methoxy-4,4-diphenyl-2,5-cyclohexadienone; 2-methoxy-4,4-diphenyl-2-cyclohexenone; 4-dichloromethyl-2-methoxy-4-methyl-2,5-cyclohexadienone

The photochemical products obtained from 2-methoxy-4,4-dimethyl-2,5-cyclohexadienone (Ia) by using a 200 W mercury lamp with methanol or benzene as a solvent in a Pyrex vessel were previously reported.[3] In this paper, we wish to report the photochemical behavior of 2-methoxy-4,4-diphenyl-2,5-cyclohexadienone (Ib), which was synthesized in our preceding study.[1]

A methanolic solution of Ib was irradiated with a 200 W mercury lamp at -3 °C to give an intractable mixture, but methyl 5-methoxy-6,6-diphenyl-3,5-hexadienoate (II) was formed in a yield of 54.6% under a 100 W mercury lamp at 10—12 °C for 1 h. Compound II exhibited a strong absorption at 1730 cm^{-1} in the infrared (IR) spectrum due to the ester group, and a double doublet signal at δ 2.57 ppm in the nuclear magnetic resonance (NMR) spectrum due to the C_2-methylene protons. The coupling constant (J) between the C_3- and C_4-vinylic protons in the NMR spectrum was 12 Hz. The base peak in the mass spectrum (MS) was m/e 234, corresponding to $M^+ -$ methyl acetate. As a by-product, 2-methoxy-4,5-diphenylphenol (III), a dienone-phenol rearrangement product,[1] was obtained in a yield of 10.1%.

In one run of the photochemical reaction of Ib in methanol, 9-(4-carbomethoxy-1-methoxy-2-butenylidene)-9*H*-fluorene (IV) was obtained as a crystalline compound in a yield of 31.9% together with III in a yield of 7.7%. Compound IV exhibited a doublet at δ 3.46 ppm due to the methylene protons and two multiplet signals at δ 8.22 and 8.68 ppm due to four aromatic protons deshielded by the ethylenic bond and the aromatic nucleus in the NMR spectrum. The formation of IV could be explained in terms of photochemical dehydrogenation. To obtain information on the structure of IV, compound IV was reduced with sodium borohydride (SBH) in ethanol to give the corresponding alcohol (V) in quantitative yield. In the NMR spectrum, the signals due to two methylene protons of V appeared at δ 2.70 and 3.90 ppm.

When a benzene solution of Ib was irradiated with a 100 W mercury lamp, 6-methoxy-5,6-diphenyl-2,4-cyclohexadienone (VI) and 1-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (VII) were given in the yield of 40.1 and 16.2%, respectively, together with the recovery of 22.8% of Ib. Both VI and VII were crystalline compounds, and exhibited strong carbonyl absorptions at 1670 and 1710 cm^{-1}, respectively, in the IR spectra. The NMR signals due to three vinylic protons of VI appeared at δ 5.58, 5.88, and 7.19 ppm as a doublet, doublet, and double doublet, respectively. Compound VII exhibited signals at δ 5.62 and 7.37 ppm as a doublet ($J=5$ Hz) and double doublet ($J=5$, 3 Hz), respectively, due to two vinylic protons, and at δ 3.47 ppm as a doublet ($J=3$ Hz) due to the bridgehead proton. In the ^{13}C-NMR spectrum of VI, a singlet signal due to the C_6 appeared at δ 69.1 ppm. To confirm the structure of VI, it was reduced with SBH in ethanol to give a tetrahydro compound, 2-methoxy-2,3-diphenyl-3-cyclohexenol (VIIIa), in a yield of 83.1%; VIIIa exhibited double doublet ($J=8$, 4 Hz) and triplet signals at δ 4.64 and 4.95 ppm due to the C_1- and C_4-protons, respectively. Compound VIIIa was derived to the corresponding *p*-nitrobenzoate (VIIIb), which showed a strong peak at *m/e* 262 and a medium peak at *m/e* 236 due to the loss of *p*-nitrobenzoic acid and the retro Diels–Alder fragmentation in the MS. The relative configuration of VIII was suggested to be as depicted in Chart 1 based on the Dreiding model and the coupling constant of the C_1-proton in the NMR spectrum. On the other hand, VI was reduced catalytically to give a tetrahydro compound, 2-methoxy-2,3-diphenylcyclohexanone (IX), and a hydrogenolysis compound, 2,3-diphenylphenol (Xa), in yields of 33.3 and 26.9%, respectively. Compound IX exhibited a triplet signal at δ 4.11 ppm due to the C_3-proton in the NMR spectrum. The coupling constant ($J=6$ Hz) of this signal revealed that the C_3-proton is equatorial, thus suggesting the C_3-phenyl group to be axial. On the basis of the Dreiding model, the C_2-phenyl group and C_2-methoxy group are equatorial and axial, respectively. The structure of Xa was confirmed by comparison of the melting point of its acetate (Xb) with that cited in the literature.[4)]

Next, the photochemical behavior of 2-methoxy-4,4-diphenyl-2-cyclohexenone (XIa), a starting material for Ib, was examined. In this case, only one product was obtained by irradiation for several hours in either methanol or benzene and with either a 100 W or a 200 W mercury lamp. In the NMR spectrum, this product exhibited a multiplet signal at δ 0.9—1.2 ppm and a singlet peak at δ 3.40 ppm, each corresponding to one proton, and the ^{13}C-NMR spectrum showed two singlet signals at δ 48.9 and 80.7 ppm and a doublet signal at δ 39.9 ppm. As regards its elemental analysis and the parent and fragment peaks in the MS, this product was coincident with XIa. As Anet[5)] had reported that irradiation of coumarin in ethanol solution produced a dimer, we suspected that this product might be a dimer of XIa. However, molecular weight measurement by the Rast method[6)] excluded this possibility. Based on these data, the structure of this product was finally concluded to be 1-methoxy-5,6-diphenylbicyclo[3.1.0]hexan-2-one (XII), not XIa or its dimer. The high-field shift in the NMR spectrum could be explained in terms of anisotropy induced by the cyclopropane ring system. Based on the molecular model, this proton may be one of the C_3-methylene protons. The reduction of XII with SBH gave an alcohol, 1-methoxy-5,6-diphenylbicyclo[3.1.0]hexan-2-ol(XIIIa), the *p*-nitrobenzoate of which (XIIIb) melted at 141—143 °C. In the NMR spectrum, XIIIa and XIIIb exhibited triplet signals at δ 4.91 ($J=8$ Hz) and 6.15 ($J=10$ Hz) ppm, respectively, due to the C_2-proton. The mechanism of formation of XII from XIa,[7)] and the mass fragmentation of XII are proposed to be as shown in Chart 2. From the mechanism and the coupling constants of the C_2-proton of XIIIa and b, the stereochemistry is suggested to be as shown in Chart 2.

2-Methoxy-4,4-dimethyl-2-cyclohexenone (XIb), a starting material of Ia, was irradiated in methanol with a 200 W mercury lamp to give only the starting material (XIb). This is consistent with the proposed mechanism for the formation of XII from XIa.

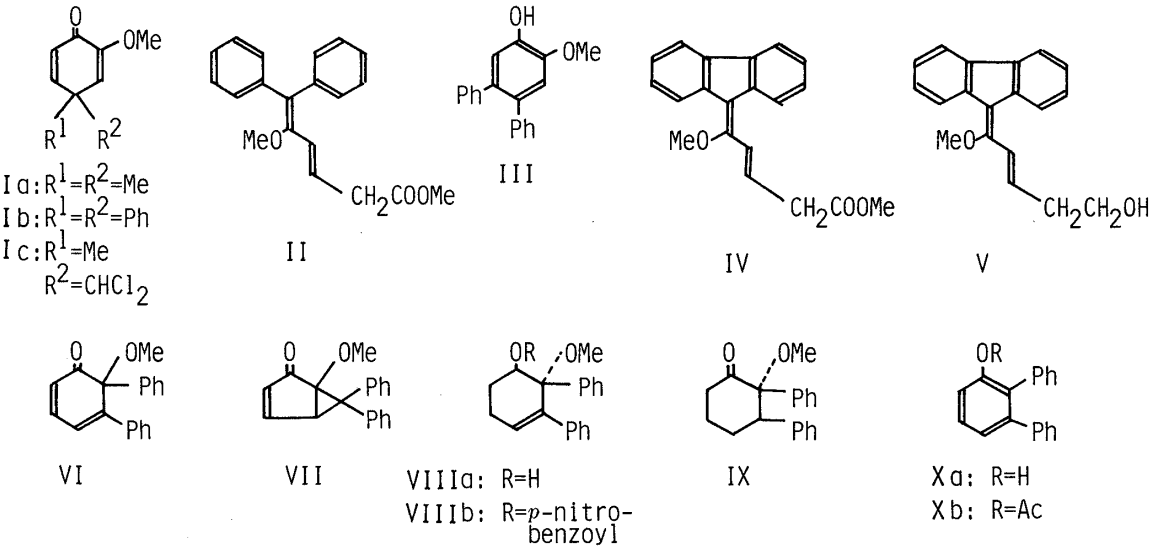

Chart 1

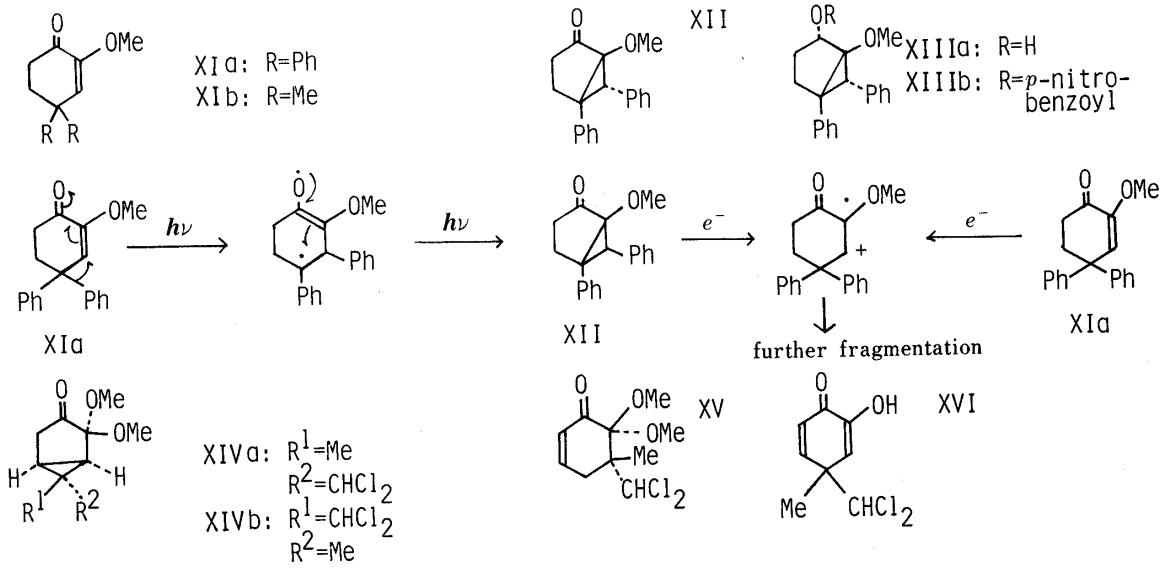

Chart 2

Finally, Ic was irradiated with a 200 W mercury lamp in methanol to give epimers at the C_6-position of 6-dichloromethyl-2,2-dimethoxy-6-methylbicyclo[3.1.0]hexan-3-one (XIVa and XIVb) and 5-dichloromethyl-6,6-dimethoxy-5-methyl-2-cyclohexenone (XV) as crystalline compounds in yield of 28.5, 11.9, and 11.2%, respectively. The separation of the epimers of XIV was effected by silica gel column chromatography. The major product was suggested on the basis of a molecular model to be XIVa, in which the C_6-dichloromethyl group is *exo*, and the minor product to be XIVb, in which this group is *endo*. Unfortunately, attempts to confirm this assignment by measuring the nuclear Overhauser effect were unsuccessful. In the NMR spectrum, the geminal coupling constants of the C_4-methylene protons of XIV and XV were 20 and 22 Hz, respectively, and the signals due to two bridgehead protons of XIVa and XIVb appeared at δ 1.77 and 1.85 ppm, respectively. The elemental analyses of these products were consistent with the formulas. When Ic was irradiated in methanol in the presence of a catalytic amount of sulfuric acid, XIVa and 4-dichloromethyl-2-hydroxy-4-methyl-2,5-cyclohexadienone (XVI), a hydrolysis product, were obtained in yield of 16.7 and 22.7%, respectively, together with recovery of 36.7% of the starting material. In the NMR spectrum

of XVI, W-type coupling ($J=4$ Hz) was observed between the C_3- and C_5-protons.

A possible mechanism for the photochemical rearrangements of Ib and Ic is shown in Chart 3.

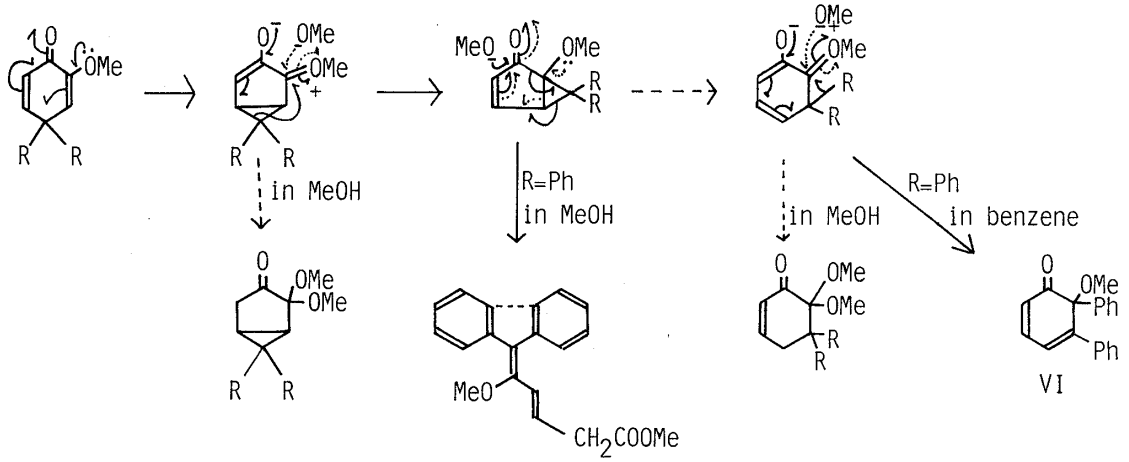

Chart 3

Experimental

All melting points (taken on a Kofler block) and boiling points (bath temperature) are uncorrected. IR spectra were determined by using a JASCO A 102 diffraction grating spectrophotometer; absorption data are given in cm^{-1}. NMR spectra were recorded on a Varian EM-360, JEOL PMX-60, Varian EM-390, or Varian XL-200 spectrometer with tetramethylsilane (TMS) as an internal standard. The chemical shifts and coupling constants (J) are given in δ and Hz, respectively. MS were measured with JEOL D-300 and D-200 (70 eV, direct inlet system) spectrometers. Ultraviolet (UV) spectra were obtained in MeOH with Hitachi 220 spectrometers, and absorption maxima are given in nm. Gas chromatography (GC) was carried out on a Shimadzu GC-6AM instrument with a stainless steel column packed with 5% SE-30. The N_2 gas flow was 40 ml/min. All solvents were removed by evaporation under reduced pressure after drying of the solution over anhyd. $MgSO_4$ or Na_2SO_4.

General Procedure for Photochemical Experiments——A methanolic or benzene solution of the starting material in a Pyrex vessel equipped with a thermometer, N_2-gas inlet system and a drying tube was well stirred and agitated for 1 h with N_2 which had been dried with anhyd. $CaCl_2$ and deoxygenated with BASF catalyst. The solution was cooled and irradiated with a mercury lamp. The irradiation was continued with monitoring by GC.

Irradiation of 2-Methoxy-4,4-diphenyl-2,5-cyclohexadienone (Ib) in MeOH——a) A methanolic solution (240 ml) of Ib (101.0 mg, 0.37 mmol) was irradiated with a 100 W mercury lamp at 10—16 °C for 1 h. After removal of MeOH, the residue was dissolved in benzene and the organic layer was washed with water. The residue obtained after removal of the solvent was fractionated through an SiO_2 column. 2-Methoxy-4,5-diphenylphenol (III) and methyl 5-methoxy-6,6-diphenyl-3,5-hexadienoate (II) were eluted successively with benzene. II: a viscous oil 61.5 mg (0.2 mmol, 54.6%). MS m/e (%): 308 (M^+, 68.0), 234 ($M^+ -$AcOMe, base peak). IR ($CHCl_3$): $\nu_{C=O}$ 1730. UV λ_{max}: 237. NMR ($CDCl_3$): 2.57 (2H, dd, $J=8$, 2, $>CH_2$), 3.47 and 3.55 (each 3H, s, OMe), 5.70 (1H, dt, $J=12$, 8, C_3-H), 6.68 (1H, dt, $J=12$, 2, C_4-H), 6.9—7.6 (10H, m, aromatic H). III (10.2 mg, 10.1%) was identified by comparison of the NMR spectrum with that of an authentic sample.[1)]

b) A methanolic solution of Ib (100.4 mg, 0.36 mmol) was irradiated with a 100 W mercury lamp at 10—12 °C for 4.5 h. The residue obtained after work-up as mentioned above was fractionated through an SiO_2 column. Elution with benzene gave III (7.7 mg, 0.028 mmol, 7.7%) and 9-(4-carbomethoxy-1-methoxy-2-butenylidene)-9*H*-fluorene (IV, 35.4 mg, 31.9%) successively. IV: mp 115—117 °C (recrystallized from Et_2O–hexane). MS m/e (%): 306 (M^+, base peak), 232 ($M^+ -$AcOMe, 87.7). NMR ($CDCl_3$): 3.46 (2H, d, $J=6$, C_4-H), 3.77 and 3.89 (each 3H, s, OMe), 6.52 (1H, dt, $J=16$, 6, C_3-H), 6.92 (1H, d, $J=16$, C_2-H), 7.61 (4H, m, aromatic H), 8.22 and 8.68 (each 2H, m, aromatic H). *Anal.* Calcd for $C_{20}H_{18}O_3 \cdot 0.7H_2O$: C, 75.32; H, 6.13. Found: C, 75.31; H, 5.89. IR (KBr): $\nu_{C=O}$ 1730. UV λ_{max}: 257, 302.

Reduction of IV with Sodium Borohydride (SBH)——SBH (122 mg, 3.2 mmol) was added to an ethanolic solution (5 ml) of IV (4.7 mg, 0.015 mmol). After being stirred for 3.5 h at room temperature (r.t), the reaction mixture was diluted with H_2O (10 ml), and AcOH was added to destroy excess SBH. The $CHCl_3$ extract was dried and evaporated to give an oily residue, which was fractionated through an SiO_2 column. IV (1.8 mg, 38%) and 9-(5-hydroxy-1-methoxy-2-pentenylidene)-9*H*-fluorene (V, 1.7 mg, 39%) were eluted successively with $CHCl_3$. V: a viscous oil MS

m/e (%): 278 (M^+, base peak), 247 ($M^+ - CH_2OH$, 17.6). NMR ($CDCl_3$): 2.70 (2H, td, $J=8$, 8, C_4-H), 3.90 (5H, m, C_5-H and OMe), 6.24 (1H, dt, $J=16$, 8, C_3-H), 6.91 (1H, d, $J=16$, C_2-H), 7.64 (4H, m, aromatic H), 8.21 and 8.69 (each 2H, m). IR ($CHCl_3$): ν_{OH} 3360.

Irradiation of Ib in Benzene——A benzene solution of Ib (100.8 mg, 0.37 mmol) was irradiated with a 100 W mercury lamp at 10—17 °C for 82 min. The residue obtained after removal of the solvent was fractionated through an SiO_2 column. 6-Methoxy-5,6-diphenyl-2,4-cyclohexadienone (VI, 40.4 mg, 0.15 mmol, 40.1%) and 1-methoxy-6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one (VII, 16.3 mg, 0.059 mmol, 16.2%) were eluted successively with benzene, and Ib (23.0 mg, 0.083 mmol, 22.8%) was eluted with AcOEt. VI: mp 196—198 °C (recrystallized from acetone–Et_2O, yellow needles). MS *m/e* (%): 276 (M^+, base peak), 261 ($M^+ - Me$, 19.6), 244 ($M^+ - MeOH$, 10.8), 233 ($M^+ - 43$, 15.7), 217 ($M^+ - 59$, 19.6), 215 ($M^+ - 61$, 25.5), 202 ($M^+ - 74$, 13.7). IR ($CHCl_3$): $\nu_{C=O}$ 1670, ν1630. UV λ_{max} (ε): 355 (2600), 244 (2500). NMR ($CDCl_3$): 3.66 (3H, s, OMe), 5.58 (1H, d, $J=8$, C_4-H), 5.88 (1H, d, $J=10$, C_2-H), 7.19 (1H, dd, $J=10$, 8, C_3-H), 7.1—7.4 (10H, m, aromatic H). ^{13}C-NMR ($CDCl_3$): 200.9 (s, C_1), 143.4 (d, C_3), 140.8 (s, C_5), 118.5 (d, C_2), 94.2 (d, C_4), 69.1 (s, C_6), 56.0 (q, OMe). *Anal.* Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.28; H, 5.79. VII: mp 175—180 °C (recrystallized from Et_2O). MS *m/e* (%): 276 (M^+, 92.2), 244 ($M^+ - MeOH$, base peak), 233 ($M^+ - 43$, 43.1), 217 ($M^+ - 59$, 35.3), 215 ($M^+ - 61$, 52.9), 202 ($M^+ - 74$, 29.4). IR ($CHCl_3$): $\nu_{C=O}$ 1710. UV λ_{max} (ε): 280 (sh., 3800). NMR ($CDCl_3$): 3.42 (3H, s, OMe), 3.47 (1H, d, $J=3$, C_5-H), 5.62 (1H, d, $J=5$, C_3-H), 7.1—7.4 (10H, m, aromatic H), 7.37 (1H, dd, $J=5$, 3, C_4-H). *Anal.* Calcd for $C_{19}H_{16}O_2 \cdot 0.3H_2O$: C, 81.01; H, 5.93. Found: C, 81.14; H, 5.65.

2-Methoxy-2,3-diphenyl-3-cyclohexenol (VIIIa)——SBH (132 mg, 3.5 mmol) was added to an ethanolic solution of VI (35.6 mg, 0.13 mmol) at r.t. After being stirred for 3.5 h at r.t., the reaction mixture was worked up as described in the case of the reduction of IV with SBH to give a viscous oily residue, which was purified through an SiO_2 column to give crude VIIIa. VIIIa: 30 mg (0.11 mmol, 83%). MS *m/e* (%): 280 (M^+, base peak), 236 ($M^+ - CH_2=CH-OH$, 56.9), 206 ($M^+ - 74$, 51.6), 205 (50.8), 167 ($M^+ - 113$, 49.0), 165 (58.8). IR ($CHCl_3$): ν_{OH} 3590, ν1660. NMR ($CDCl_3$): 1.7—1.9 (2H, m, C_6-H), 2.32 (2H, m, C_5-H), 3.58 (3H, s, OMe), 4.64 (1H, dd, $J=10$, 4, C_1-H), 4.95 (1H, t, $J=4$, vinylic H), 7.2—7.5 (10H, m, aromatic H).

VIIIa-*p*-Nitrobenzoate (VIIIb): mp 210—211 °C (recrystallized from Et_2O–hexane). MS *m/e* (%): 430 ($M^+ + 1$, 0.9), 429 (M^+, 2.9), 262 ($M^+ - p$-nitrobenzoic acid, base peak), 236 ($M^+ - CH_2=CH-OCO-C_6H_4-NO_2$, 37.3), 235 (47.1), 205 ($M^+ - 225$, 27.5). High-resolution MS: Calcd for $C_{18}H_{16}NO$: 262.1231. Found: 262.1281. NMR ($CDCl_3$): 1.8—2.1 and 2.3—2.5 (each 2H, m, CH_2–CH_2), 3.53 (3H, s, OMe), 5.06 (1H, t, $J=4$, vinylic H), 6.20 (1H, dd, $J=8$, 4, C_1-H), 7.2—7.5 (10H, m, aromatic H), 8.04 and 8.23 (each 2H, A_2B_2 type, $J=8$, aromatic H).

Catalytic Reduction of VI——A solution of VI (71.1 mg, 0.26 mmol) in MeOH–AcOEt (1 : 2, 30 ml) was shaken in the presence of PtO_2 (0.1 g) in an atmosphere of H_2 under normal pressure at r.t. for 1.5 h. After removal of the catalyst by filtration, the filtrate was concentrated to give an oily residue, which was purified through an SiO_2 column. 2,3-Diphenylphenol (Xa, 19.1 mg, 0.070 mmol, 26.9%) and 2-methoxy-2,3-diphenylcyclohexanone (IX, 24.0 mg, 0.086 mmol, 33.3%) were eluted successively with benzene. IX: mp 155—157 °C (recrystallized from Et_2O–hexane). MS *m/e* (%): 281 ($M^+ + 1$, 21.6), 280 (M^+, 90.2), 209 ($M^+ - 71$, 49.0), 165 ($M^+ - 115$, 39.2), 71 ($C_3H_7C\equiv O^+$, base peak). IR (KBr): $\nu_{C=O}$ 1710, $\nu_{C=C}$ 1600 (weak). NMR ($CDCl_3$): 1.6—1.8 and 1.9—2.1 (each 1H, m),2.17 (2H, td, $J=6$, 6, C_4-H), 2.44 (2H, t, $J=6$, C_6-H), 3.06 (3H, s, OMe), 4.11 (1H, t, $J=6$, C_3-H), 7.00 (2H, dd, $J=8$, 4, aromatic H), 7.1—7.3 (8H, m, aromatic H). *Anal.* Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.44; H, 7.05. Xa: MS *m/e* (%): 247 ($M^+ + 1$, 19.6), 246 (M^+, base peak), 245 ($M^+ - 1$, 22.5), 227 ($M^+ - 19$, 21.6). NMR ($CDCl_3$): 5.07 (1H, s, –OH), 6.9—7.4 (13H, m).

Xa-acetate (Xb): mp 114—117 °C (Lit.[4] mp 117.5—118 °C).

Irradiation of 2-Methoxy-4,4-diphenyl-2-cyclohexenone (XI)——A methanolic solution (240 ml) of XI (119.6 mg, 0.72 mmol) was irradiated with a 100 W mercury lamp at 8—17 °C for 2 h. The residue obtained after work-up in the usual manner was purified through an SiO_2 column. 1-Methoxy-5,6-diphenylbicyclo[3.1.0]hexan-2-one (XII, 126.8 mg, 0.46 mmol, 63.5%) and XI (26.3 mg, 0.095 mmol, 13.2%) were eluted successively with benzene–5% AcOEt. XII: mp 137–139 °C (recrystallized from Et_2O). MS *m/e* (%): 279 ($M^+ + 1$, 33.3), 278 (M^+, 68.6), 250 ($M^+ - 28$, 13.7), 236 ($M^+ - CH_2$–CO, 39.2), 219 ($M^+ - 59$, 92.2), 204 ($CH\equiv C-CH=CPh_2$, base peak). IR ($CHCl_3$): $\nu_{C=O}$ 1720. NMR ($CDCl_3$): 0.9—1.2 (1H, m, C_3-*endo* H), 1.9—2.2 (2H, m), 2.3—2.5 (1H, m), 3.40 (1H, s, C_6-H), 3.57 (3H, s, OMe), 7.2—7.5 (10H, m, aromatic H). *Anal.* Calcd for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 81.93; H, 6.68.

Molecular weight determination by the Rast method[6]: the sample was prepared from camphor (51.3 mg) and XII (5.0 mg). The observed average depression of the mp was 18.1 °C. The calculated molecular weight was 215. ^{13}C-NMR ($CDCl_3$): 26.5 (t, C_4), 33.1 (t, C_3), 39.9 (d, C_6), 48.9 (s, C_5), 58.3 (q, OMe), 80.7 (s, C_1), 127.4—140.6 (aromatic C), 211.2 (s, C_2).

1-Methoxy-5,6-diphenylbicyclo[3.1.0]hexan-2-ol (XIIIa)——SBH (60.9 mg, 1.6 mmol) was added to an ethanolic solution of XII (119.4 mg, 0.43 mmol) at r.t. The mixture was stirred for 2 h at r.t. and then worked up in the usual manner to give pure XIIIa. XIIIa: 63.4 mg (91.7%). Oily substance. MS *m/e* (%): 280 (M^+, 9.8), 262 ($M^+ - H_2O$, 9.8), 236 ($M^+ - CH_2=CH-OH$, base peak), 235 (31.4). IR ($CHCl_3$): ν_{OH} 3400, 3560. NMR ($CDCl_3$): 0.4—0.5 (1H, m), 1.7—1.9 (1H, m), 2.0—2.3 (2H, m), 2.94 (1H, s, C_6-H), 3.66 (3H, s, OMe), 4.91 (1H, t, $J=8$), 7.2—7.7 (10H, m,

aromatic H).

XIIIa-*p*-Nitrobenzoate (XIIIb): mp 141—143 °C (recrystallized from Et_2O). NMR ($CDCl_3$): 1.4—1.5 (1H, m, C_3-*endo* H), 2.0—2.5 (3H, m), 3.13 (1H, s, C_6-H), 3.56 (3H, s, OMe), 6.15 (1H, t, $J=10$, C_2-H), 7.1—7.7 (10H, m, aromatic H), 8.26 and 8.37 (each 2H, A_2B_2 type, $J=8$, aromatic H).

Irradiation of 4-Dichloro-2-methoxy-4-methyl-2,5-cyclohexadienone (Ic)——A methanolic solution (200 ml) of Ic (568.5 mg, 2.57 mmol) was irradiated with a 200 W mercury lamp at −5 °C for 31 h. The residue obtained after work-up in the usual manner was crystallized and recrystallized from hexane to give 6-*exo*-dichloromethyl-2,2-dimethoxy-6-methylbicyclo[3.1.0]hexan-3-one (XIVa). XIVa: mp 100—102 °C. NMR ($CDCl_3$): 1.30 (3H, s, C_6-Me), 1.77 (2H, d like $J=4$, C_1- and C_5-H), 2.30 (1H, d, $J=20$, C_4-*endo* H), 2.77 (1H, dt, $J=20$, 4, C_4-*exo* H), 3.24 and 3.45 (each 3H, s, OMe), 5.13 (1H, s, $CHCl_2$). *Anal.* Calcd for $C_{10}H_{14}Cl_2O_3$: C, 47.45; H, 5.58. Found: C, 47.24; H, 5.53. The residue obtained after removal of the mother liquor of recrystallization of XIVa was fractionated through an SiO_2 column with benzene as an eluant. The first eluate was recrystallized from hexane to give a mixture of XIVa and 6-*endo*-dichloromethyl-2,2-dimethoxy-6-methylbicyclo[3.1.0]hexan-3-one (XIVb) (1 : 4, 96.9 mg). mp 51—64 °C. *Anal.* Calcd for $C_{10}H_{14}Cl_2O_3$: C, 47.45; H, 5.58. Found: C, 47.59; H, 5.52. NMR of XIVb ($CDCl_3$): 1.47 (3H, s, C_6-Me), 1.85 (2H, m, C_1- and C_5-H), 2.55 (1H, d, $J=20$, C_4-*endo* H), 2.85 (1H, dt, $J=20$, 1.5, C_4-*exo* H), 3.25 and 3.44 (each 3H, s, OMe), 5.37 (1H, s, $CHCl_2$). The yields of XIVa and XIVb were 186.1 mg (28.5%) and 77.5 mg (11.9%), respectively. The later eluate from SiO_2 column chromatography was micro-distilled to give 5-dichloromethyl-6,6-dimethoxy-5-methyl-2-cyclohexenone (XV, 72.7 mg, 11.2%). bp <120 °C (0.15 mmHg), NMR ($CDCl_3$): 1.24 (3H, s, C_5-Me), 2.88 and 3.06 (each 1H, dm, $J=22$, C_4-H), 3.20 and 3.50 (each 3H, s, OMe), 5.57 (1H, dt, $J=10.5$, 2.0, C_2-H), 5.78 (1H, s, $CHCl_2$), 5.91 (1H, dt, $J=10.5$, 3.0). *Anal.* Calcd for $C_{10}H_{14}Cl_2O_3$: C, 47.45; H, 5.58. Found: C, 47.69; H, 5.62.

Irradiation of Ic in MeOH in the Presence of H_2SO_4——A methanolic solution (200 ml) of Ic (201.1 mg, 0.91 mmol) and conc. H_2SO_4 (1 drop) was irradiated with a 100 W mercury lamp at 5 °C for 22 h. After being worked up as usual, the residue was fractionated through an SiO_2 column. 4-Dichloromethyl-2-hydroxy-4-methyl-2,5-cyclohexadienone (XVI, 42.8 mg, 0.21 mmol, 22.7%), XIV (38.4 mg, 0.15 mmol, 16.7%), and Ic (73.9 mg, 36.7%) were eluted with benzene, benzene, and $CHCl_3$, respectively. XVI: mp 92—93 °C (recrystallized from hexane). MS, *m/e* (%): 210 ($M^+ +4$, 0.9), 208 ($M^+ +2$, 4.9), 206 (M^+, 7.8), 123 ($M^+ - CHCl_2$, base peak). NMR ($CDCl_3$): 1.51 (3H, s, C_4-Me), 5.69 (1H, s, $-CHCl_2$), 6.15 (1H, d, $J=4$, C_3-H), 6.39 (1H, s, –OH), 6.52 (1H, d, $J=10$, C_6-H), 6.87 (1H, dd, $J=10$, 4, C_5-H). *Anal.* Calcd for $C_8H_8Cl_2O_2$: C, 46.51; H, 3.89. Found: C, 46.26: H, 3.89.

References and Notes

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