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Chemistry of 2-Methoxy-2,5-cyclohexadienones. I. Photochemistry of 2-Methoxy-4,4-dimethyl-2,5-cyclohexadienone[1]

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The title compound, 2-methoxy-4,4-dimethyl-2,5-cyclohexadienone (V), was prepared from 2-methoxy-4,4-dimethyl-2-cyclohexenone (VIa). A methanolic solution of V was irradiated with a 200 W mercury lamp at −3°C to give 2,2-dimethoxy-6,6-dimethylbicyclo[3.1.0]hexan-3-one (X) and 6,6-dimethoxy-5,5-dimethyl-2-cyclohexenone (XI) in yields of 36.5 and 7.8%, respectively.

On the other hand, a methanolic solution of V was irradiated in the presence of a catalytic amount of sulfuric acid to give only 2-methoxy-4-(1-methoxy-1-methylethyl)-2-cyclopentenone (XIII) in 35.4% yield.

The behavior of V and VIa in the presence of a catalytic amount of acid is also described.

Keywords——cyclohexadienone; 2-methoxy-2,5-cyclohexadienone; photochemistry; acid-isomerization; bicyclo[3.1.0]hexan-3-one

It has been found that the 2-methoxy-2,5-cyclohexadienone moiety is involved in a number of natural products, such as salutalidine(I), androcymbine(II), and (±)kreysiginone(III). This moiety also plays an important biogenetic role.[2] In fact, a few natural alkaloids have been synthesized *via* biomimetic routes from compounds containing this moiety,[3] and Barton *et al.*[4] proposed an interesting biogenetic route to acutumine(IV) from 4-spiro-2-methoxy-2,5-cyclohexadienone. From this point of view, the chemistry of 2-methoxy-2,5-cyclohexadinone was examined.

Zimmerman *et al.*[5] reported on the photochemical behavior of the 3-methoxy- or 3-cyano-2,5-cyclohexadienone system. In this connection, we will describe the photochemical products obtained from 2-methoxy-4,4-dimethy-2,5-cyclohexadienone(V), which was synthesized from 2-methoxy-4,4-dimethyl-2-cyclohexenone(VIa). VIa was prepared by two methods. One was Wenkert's method[6] and the other was a route *via* 2,3-epoxy-4,4-dimethylcyclohexanone.[7] In the former method, 6-isobutylidene-2-methoxy-2-cyclohexenone(VII) was formed as an undesired product. An attempt to convert VII into VIa under basic conditions (sodium methoxide or potassium hydroxide in methanol) was made, but the starting material was recovered. In the latter case, VIa could be obtained in a yield of 36.8%. VIa exhibited a singlet signal at δ 5.50 due to the vinylic proton in the nuclear magnetic resonance (NMR) spectrum. When VIa was treated with boron trifluoride(BF_3)-etherate, a mixture of unchanged VIa and its isomer, 2-methoxy-5,5-dimethyl-2-cyclohexenone(VIb), was obtained. VIb exhibited a triplet signal at δ 5.62 due to the vinylic proton in the NMR spectrum. The ratio of VIa and VIb was calculated from the results of integration of the vinylic protons in the NMR spectrum, and it was about 23 : 77 when VIa was refluxed for 1 h with the Lewis acid in methanol. The ratio did not change on prolonged heating. The ratio was the same as that obtained when concentrated sulfuric acid was used instead of BF_3-etherate. When an ethanolic solution of VIa was refluxed in the presence of the Lewis acid, it gave a mixture of 2-ethoxy-4,4-dimethyl-2-cyclohexenone(VIIIa) and 2-ethoxy-5,5-dimethyl-2-cyclohexenone(VIIIb) in the ratio of 1 : 3. This result suggested that the transformation from VIa to VIb in methanol was an intermolecular rather than an intramolecular reaction. In the oxidation of VIa to V, selenium dioxide or 2,3-dichloro-5,6-dicyano-1,4-benzoquinone(DDQ) was used. In the former case, bis[6-(2-methoxy-4,4-dimethyl-2,5-cyclohexadienone)selenide](IX) was obtained in a yield of 5.3% as a by-product. The NMR spectrum of IX showed a long-range coupling (J=2.8 Hz) between the two vinylic protons. In the latter case, the work-up procedures were simpler and the yield of V was better than in the former case. The physical data for V were in accord with those described in the literature.[6]

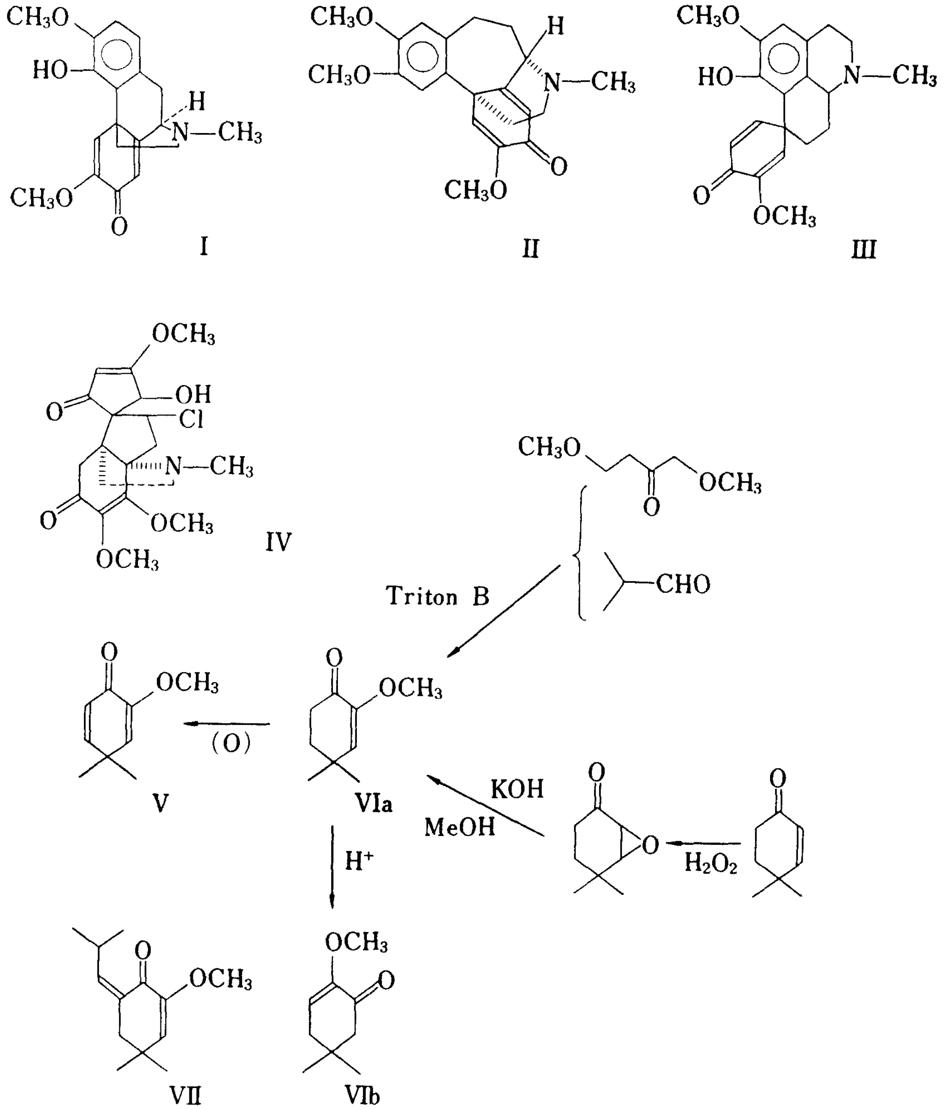

Chart 1

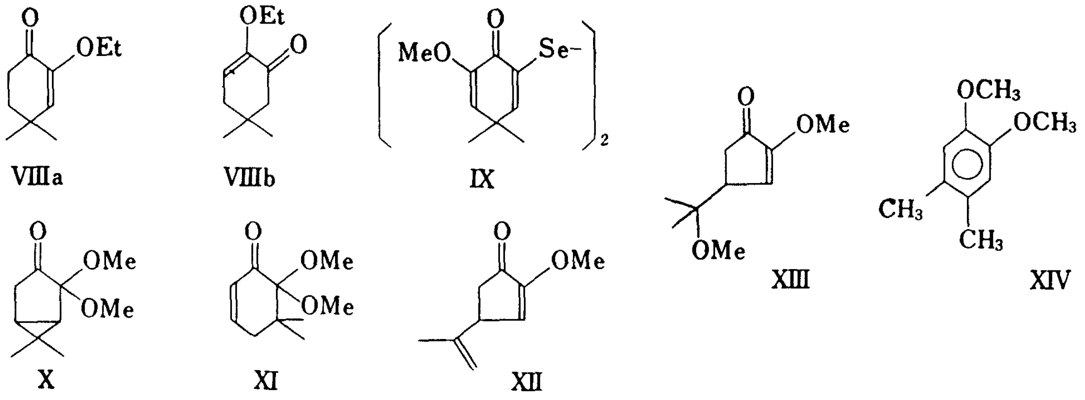

Chart 2

Next, a photochemical reaction was carried out on V. A Pyrex glass vessel was used and the temperature was maintained at −3 °C. The light source was a 200 W mercury lamp. In methanol, 2,2-dimethoxy-6,6-dimethyl-bicyclo[3.1.0]hexan-3-one(X) and 6,6-dimethoxy-5,5-dimethyl-2-cyclohexenone(XI) were obtained in yields of 36.5 and 7.8%, respectively. X exhibited a carbonyl absorption at 1755 cm^{-1} in the infrared (IR) spectrum, and in the NMR spectrum of X, a triplet-like signal found at near δ 1.44 was considered to be due to two protons at the bridgehead position, which coupled with the coupling constants (J) of 3.5 and 2.0 Hz with one of the methylene protons of the C_4-position. The assignment was supported by a decoupling experiment. XI exhibited a carbonyl absorption at 1695 cm^{-1} in the IR spectrum and gave a doublet of triplets due to the C_3-proton at δ 6.80 in the NMR spectrum. To confirm the structure of X, it was treated with *p*-toluenesulfonic acid in benzene to give 4-isopropenyl-2-methoxy-2-cyclopentenone(XII) in 54% yield. XII exhibited a carbonyl band at 1733 cm^{-1} in the IR spectrum and a singlet signal at δ 4.83 ascribed to the terminal methylene in the NMR spectrum. The formulae of X, XI, and XII were confirmed by their high resolution mass spectra (MS).

On the other hand, when a methanolic solution of V was irradiated in the presence of a catalytic amount of concentrated sulfuric acid, 2-methoxy-4-(1-methoxy-1-methylethyl)-2-cyclopentenone(XIII) was obtained in 35.4% yield. In this case, X and XI, which were obtained in the absence of acid, could not be detected by gas chromatography throughout the reaction. However, when X was treated with acidic methanol in a dark room at 3.5°C, it gave XIII in 53.4% yield. Thus, it appears that X was an intermediate in the formation of XIII from V, and the rate of acid isomerization of X to XIII was fast. XIII exhibited a carbonyl band at 1740 cm^{-1} in the IR spectrum and a doublet signal at δ 6.37 due to the vinylic proton at the C_3-position in the NMR spectrum. The formula of XIII was confirmed by analysis of the 2,4-dinitrophenylhydrazone. To avoid the possibility of the formation of XIII from V in a dark reaction, a control experiment was carried out at 3.5°C in the presence of a catalytic amount of acid; the starting material was recovered unchanged. The interconversion between XII and XIII was tried under acidic and basic conditions (sodium methoxide and BF_3-etherate in methanol). However, appropriate conditions could not be found.

To examine the photochemical product from V in benzene, a solution of V was irradiated at 8°C for 10 h to yield mainly the unchanged starting material and a small amount of a mixture of unpurifiable material. A possible mechanism for the formation of these photochemical products is shown in Chart 3.

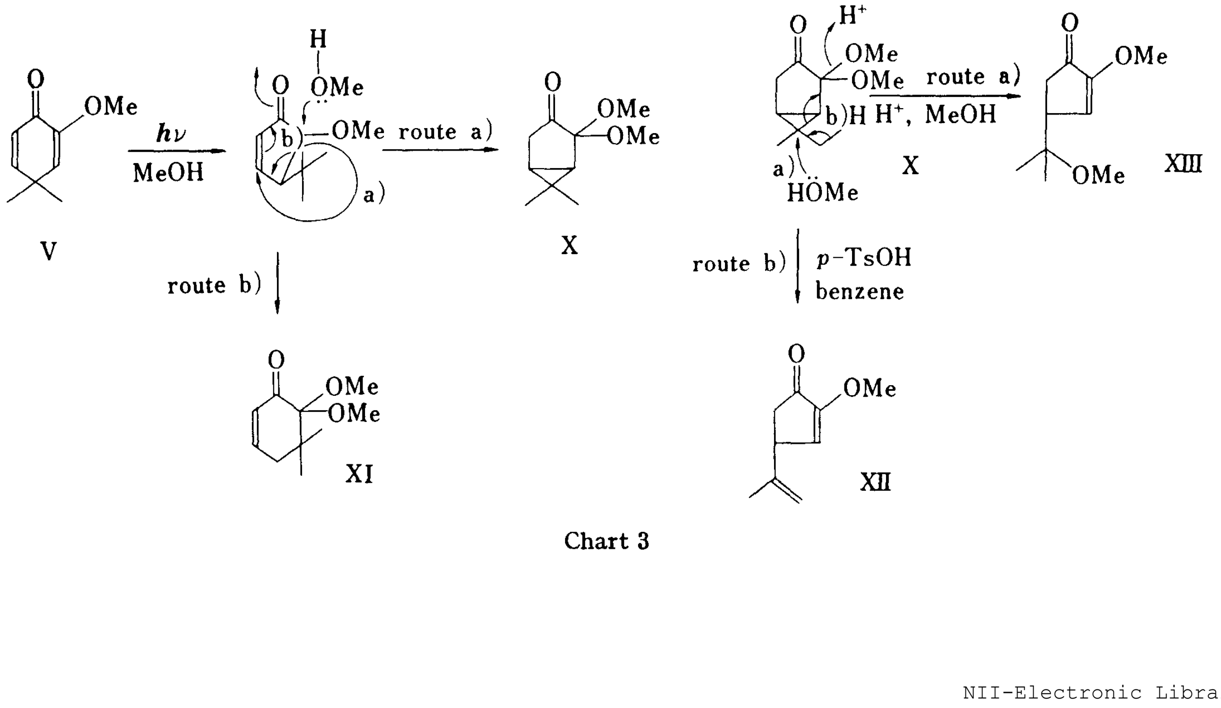

Chart 3

The dienone–phenol rearrangement of V was also examined by using BF_3-etherate. A methanolic solution of V was refluxed in the presence of acid to give 1,2-dimethoxy-4,5-dimethylbenzene(XIV), the structure of which was suggested from mechanistic considerations and confirmed by the NMR spectrum and elemental analysis results.

Experimental

All melting points are uncorrected. IR spectra were determined by using a Hitachi 215 grating spectrophotometer or a JASCO IRA-1 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 TMS as an internal standard. The chemical shifts and coupling constants (J) are given in δ and Hz, respectively. Mass spectra were measured with a JEOL D-200 (70 eV, direct inlet system) spectrometer. Ultraviolet (UV) spectra were obtained in MeOH with a Hitachi 200-10 spectrophotometer, and absorption maxima are given in nm. All solvents were removed by evaporation under reduced pressure.

2-Methoxy-4,4-dimethyl-2-cyclohexenone (VIa)——Purified 2,3-epoxy-4,4-dimethyl cyclohexanone8) (1 g, 7.14 mmol) was added to methanolic KOH (466 mg, 7.16 mmol), and the mixture was allowed to stand overnight. After being refluxed for 2.5 h, the reaction mixture was poured into ice-water (70 ml) and extracted with Et_2O three times, and the combined Et_2O layer was washed with brine, dried and concentrated. The oil obtained was separated into a hexane-soluble part and hexane-insoluble part. From the former part, VIa was obtained. bp 85—91°C (2 mmHg). The yield was 405 mg (36.8%). NMR ($CDCl_3$): 1.23 (s, 6H), 1.87 (t, 2H, $J=6$), 2.61 (t, 2H, $J=6$), 3.60 (s, 3H), 5.59 (s, 1H). [Lit.6) ($CDCl_3$): 1.19 (s, 6H), 1.82 (t, 2H, $J=6$), 2.56 (t, 2H, $J=6$), 3.56 (s, 3H), 5.52 (s, 1H).]

6-Isobutylidene-2-methoxy-4,4-dimethyl-2-cyclohexenone (VII)——Isobutyraldehyde (21.9 g, 0.3 mol) and 38% methanolic Triton B (30.4 g) in MeOH (250 ml) were successively added dropwise to 1,4-dimethoxy-2-butanone (40 g, 0.3 mol) in a 500 ml three-necked flask with mechanical stirring. After being refluxed for 13 h, the mixture was concentrated and diluted with water. The aq. solution was extracted several times with Et_2O. The combined Et_2O extract was dried, concentrated, and then distilled. bp 112—123°C (6 mmHg). 17.1 g. The distillate was purified through an SiO_2 column. VII and VIa were eluted with 10% AcOEt–hexane and 20% AcOEt–hexane, and the yields of VII and VIa were 13.7 and 18.5%, respectively. VII: bp <155°C (4 mmHg). IR (film): 1675, 1630. NMR ($CDCl_3$): 1.08 (d, 6H, $J=7$), 1.24 (s, 6H), 1.53—1.93 (m, 1H), 2.53 (s, 2H), 3.65 (s, 3H), 5.70 (s, 1H, C_3–H), 6.58 (d, 1H, $J=10$). MS m/e (%): 209 ($M^+ +1$, 11.5), 208 (M^+, 78), 193 ($M^+ - CH_3$, base peak), 165 ($M^+ -$propyl, 24). *Anal.* Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.39; H, 9.55. *cf*; Calcd for $C_{13}H_{20}O_2 + 1/10H_2O$: C, 74.32; H, 9.69.

2-Methoxy-5,5-dimethyl-2-cyclohexenone (VIb)——BF_3 etherate (1 ml) was added to a methanolic solution of VIa (0.1 g), and the mixture was refluxed for 1 h, then concentrated. The resulting mixture was basified with 10% NH_4OH solution. The Et_2O extract was dried and concentrated to give an oily material (105 mg, VIa: VIb=23: 77), which was purified through an SiO_2 column. VIa and VIb were eluted succ essivelywith20% AcOEt–hexane, but VIb could not be obtained in a pure state. VIa+VIb: bp <110 °C (4 mmHg). IR (film): $\nu_{C=O}$ 1750 (weak), 1690, ν 1630. MS m/e (%): 154 (M^+, 58.5), 139 ($M^+ - CH_3$, 48.6), 111 (m/e 139$-$CO, 44.9), 98 (53), 70 (58.9), 55 (base peak). *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.10; H, 9.15. Found: C, 69.46; H, 9.14. *cf*; Calcd for $C_9H_{14}O_2 + 1/15\ H_2O$: C, 69.56; H, 9.17. NMR (CCl_4, peaks ascribed to VIb): 1.13 (s, 6H), 2.24 (s, 2H), 2.32 (d, 2H, $J=4.6$), 3.60 (s, 3H), 5.62 (t, 1H, $J=4.6$). The product ratio was estimated from the NMR spectrum, and did not change significantly on prolonged heating of the products with BF_3-etherate in MeOH.

2-Ethoxy-4,4-dimethyl-2-cyclohexenone (VIIIa) and 2-Ethoxy-5,5-dimethyl-2-cyclohexenone (VIIIb)——BF_3-etherate (1 ml) was added to an ethanolic solution of VIa (0.5 g). The reaction and the work-up were carried out in a manner similar to that used for the isomerization of VIa in MeOH. The crude product (0.59 g) was micro-distilled. VIIIa+VIIIb (1: 3): bp <120°C (11 mmHg). NMR (CCl_4): 5.50 (s, C_3–H of VIIIa), 5.62 (t, $J=4.4$, C_3–H of VIIIb). *Anal.* Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.92; H, 9.55. *cf*; Calcd for $C_{10}H_{16}O_2 + 1/20\ H_2O$: C, 71.02; H, 9.60.

VIIIa was also prepared in 16.4% yield from 2,3-epoxy-4,4-dimethylcyclohexanone by treatment with KOH in EtOH in a manner similar to that used in the preparation of VIa. NMR ($CDCl_3$): 1.21 (s, 6H), 1.37 (t, 3H, $J=7$), 1.86 (t, 2H, $J=6.6$), 2.58 (t, 2H, $J=6.6$), 3.75 (q, 2H, $J=7$), 5.52 (s, 1H).

2-Methoxy-4,4-dimethyl-2,5-cyclohexadienone (V)——1) With SeO_2: A mixture of VIa (3.56 g, 23.1 mmol), 95% SeO_2 (3.26 g, 27.9 mmol), AcOH (25.5 ml), and anhyd. *tert*-amyl alcohol (199 ml) was refluxed for 36.5 h. An oily crystalline product obtained after work-up as described in the literature9) was washed with Et_2O and separated into an Et_2O-insoluble crystalline compound and an Et_2O-soluble oil (3.35 g). The former compound (0.42 g) was recrystallized from EtOH to give yellow needles of bis[6-(2-methoxy-4,4-dimethyl-2,5-cyclohexadienone)selenide] (IX). mp 224.5—227°C. IR (Nujol): $\nu_{C=O}$ 1645, $\nu_{C=C}$ 1604. NMR ($CDCl_3$): 1.27 (s, 12H), 3.69 (s, 6H), 5.87 (d, 2H, $J=2.8$), 6.87 (d, 2H, $J=2.8$). MS m/e (%): 464 ($M^+ +2$, 3.3), 464 (M^+, 9.5), 460 ($M^+ -2$, 8.5), 458 ($M^+ -4$, 5.5), 231 (monomer, 12.6), 152 (V, 50.0), 151 (V$-$1, base peak). *Anal.* Calcd for $C_{18}H_{22}O_4Se_2$: C, 46.97; H, 4.81. Found: C, 46.72; H, 4.81.

The latter oil was purified through an Al_2O_3 column. VIa (0.49 g), V (1.66 g, yield: 47.2%), and IX (0.16 g, total 0.58 g, 5.3%) were eluted successively with hexane–Et_2O. V: NMR ($CDCl_3$): 1.34 (s, 6H), 3.68 (s, 3H), 5.78 (d, 1H, $J=3$, C_3–H), 6.20 (d, 1H, $J=10$, C_6–H), 6.87 (dd, 1H, $J=10$, 3, C_5–H). [Lit.[9] 1.31 (s, 6H), 3.62 (s, 3H), 5.76 (d, 1H, $J=2$), 6.18 (d, 1H, $J=10$), 6.79 (dd, 1H, $J=10$, 2)].

2) With DDQ:[10] A dioxane solution of VIa (0.5 g, 3.3 mmol) and DDQ (1 g, 4.0 mmol) was refluxed with stirring for 30 h, then filtered. The filtrate was concentrated. The residue was rinsed with Et_2O, and the Et_2O layer was washed with 10% NaOH and brine. A deep-yellow oil (415 mg) was obtained by removal of the solvent, and was distilled. bp <156°C (11 mmHg). The yield was 260 mg (51.5%).

General Procedure for Photochemical Experiments——A solution of V 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 H_2SO_4 and deoxygenated with BASF catalyst). The solution was cooled at −3°C and irradiated with a mercury lamp (200 W). The irradiation was continued until the starting material could no longer be detected by gas chromatography.

2,2-Dimethoxy-6,6-dimethylbicyclo[3.1.0]hexan-3-one (X) and 6,6-Dimethoxy-5,5-dimethyl-2-cyclohexenone (XI)——A methanolic solution (200 ml) of V (395 mg, 2.6 mmol) was irradiated for 8 h. The orange oil (325 mg) obtained by removal of the solvent was purified through an Al_2O_3 column. X (175 mg, 36.5%) and XI (38 mg, 7.8%) were obtained from the eluates with hexane–Et_2O (9: 1) and (4: 1), respectively. X: IR (film): $\nu_{C=O}$ 1755. NMR ($CDCl_3$): 1.02 (s, 3H), 1.14 (s, 3H), 1.436 (d, 1H, $J=3.5$, C_5–H), 1.441 (d, 1H, $J=2$, C_1–H), 2.35 (d, 1H, $J=20$, C_4–H), 2.82 (ddd, $J=20$, 3.5, 2.0, C_4–H), 3.28 (s, 3H), 3.45 (s, 3H). MS *m/e* (%): 184 (M^+, 0.9), 156 (M^+-CO, 95.2), 153 (M^+-OCH_3, 44.5), 141 ($M^+-CO-CH_3$, base peak), 125 (*m/e* $141-OCH_3$, 29.5), 95 (*m/e* $125-CH_3$, 38.0). High resolution MS, Calcd for $C_{10}H_{16}O_3$: *m/e* 184.1098. Found: *m/e* 184.1141. XI: IR (film): $\nu_{C=O}$ 1695., δ_{C-O} 1110, 1085. NMR ($CDCl_3$): 1.11 (s, 6H), 2.33 (br s, 2H), 3.38 (s, 6H), 5.99 (d, 1H, $J=10$, C_2–H), 6.80 (dt, 1H, $J=10$, 3, C_3–H). MS *m/e* (%): 184 (M^+, 0.5), 156 (M^+-CO, 3.3), 153 (M^+-OCH_3, 7.6), 141 (*m/e* $156-CH_3$, 8.8), 116 ($M^+-C_5H_8$, base peak). High resolution MS, Calcd for $C_{10}H_{16}O_3$: *m/e* 184.1098. Found: *m/e* 184.1158.

4-Isopropenyl-2-methoxy-2-cyclopentenone (XII)——An aq. solution (1 ml) of *p*-TsOH (10 mg) was added to a benzene solution (10 ml) of X (45 mg, 0.24 mmol). After being stirred and refluxed for 4 h, the mixture was washed three times with brine then dried. An oily substance (35 mg) obtained by removal of the solvent was purified through an SiO_2 column. XII (20 mg, 54%) was obtained from the benzene–AcOEt (9: 1) eluate. IR (film): $\nu_{C=O}$ 1733, $\nu_{C=C}$ 1635, 1615. NMR ($CDCl_3$): 1.54 (s, 3H), 2.06 (dd, 1H, $J=$ 20, 2.8, C_5–H), 2.58 (dd, 1H, $J=20$, 7.2, C_5–H), 3.30—3.46 (m, 1H, C_4–H), 3.71 (s, 3H), 4.83 (s, 2H, terminal CH_2), 6.38 (d, 1H, $J=2.8$, C_3–H). MS *m/e* (%): 153 (M^++1, 10.4), 152 (M^+, base peak), 137 (M^+-CH_3, 66.1), 109 (*m/e* $137-CO$, 57.6). High resolution MS, Calcd for $C_9H_{12}O_2$: *m/e* 152.0836. Found: *m/e* 152.0179.

2-Methoxy-4-(1-methoxy-1-methylethyl)-2-cyclopentenone (XIII)——a) A solution of V (0.2 g) was irradiated in MeOH (200 ml)–conc. H_2SO_4 (1 drop). After being irradiated for 21.5 h, the mixture was neutralized with Et_3N and concentrated. The residue was dissolved in Et_2O–H_2O and the solution was washed twice with brine. The dried Et_2O layer was concentrated and the residue (pale-orange oil) was purified through an SiO_2 column. XIII was eluted with benzene–AcOEt (4: 1). The yield was 85 mg (35.4%). XIII: IR (film): $\nu_{C=O}$ 1740, $\nu_{C=C}$ 1623, δ_{C-O} 1117, 1063. UV, λ_{max} 251. NMR ($CDCl_3$): 1.10 (s, 3H), 1.14 (s, 3H), 2.25 (dd, 1H, $J=19.6$, 4.9, C_5–H), 2.45 (dd, 1H, $J=19.6$, 6.4, C_5–H), 2.93—3.04 (m, 1H, C_4–H), 3.25 and 3.75 (each s, 3H, OCH_3), 6.37 (d, 1H, $J=4$, C_3–H). MS *m/e* (%): 185 (M^++1, 0.8), 184 (M^+, 0.2), 153 (M^+-OCH_3, 30.9), 125 (*m/e* $153-CO$, 14.7), 73 (Me_2C^+-OCH_3, base peak). XIII-2,4-dinitrophenylhydrazone was recrystallized from EtOH. mp 152.5—155°C. *Anal.* Calcd for $C_{16}H_{20}N_4O_6$: C, 52.74; H, 5.53; N, 15.38. Found: C, 52.66; H, 5.57; N, 15.49.

b) A methanolic solution (20 ml) of X (23.5 mg) and conc. H_2SO_4 (1/10 drop) was stirred for 19 h at 3.5°C under an Ar atmosphere. After being neutralized with Et_3N (0.25 ml), the solution was concentrated then diluted with Et_2O. The organic layer was washed with brine and dried. After removal of solvent, the residue was analyzed by means of NMR spectroscopy and concluded to be XIII. The yield was 12.9 mg (53.4%).

Control Experiment, Reaction of V with Methanolic Sulfuric Acid——A methanolic solution (20 ml) of V (20 mg) and conc. H_2SO_4 (1/10 drop) was stirred overnight at 3.5°C. The reaction mixture was neutralized with Et_3N and concentrated. The residue was dissolved in Et_2O and the Et_2O layer was washed with brine then dried. The oily material obtained after removal of the solvent was concluded on the basis of the NMR spectrum to be V (10 mg).

1,2-Dimethoxy-4,5-dimethylbenzene (XIV)——BF_3-etherate (1 ml) was added to a methanolic solution of V (0.3 g) and the mixture was refluxed for 1 h. After being neutralized with sat. $NaHCO_3$, the mixture was extracted with Et_2O. The organic layer was dried and the solvent was removed. The residue (0.31 g) was crystallized and recrystallized from aq. EtOH. mp 41—41.8°C (Lit.[11] mp 41—43°C). The yield was 256 mg (78.2%). NMR (CCl_4): 2.12 (s, 6H), 3.68 (s, 6H), 6.49 (s, 2H). *Anal.* Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.47. Found: C, 72.14; H, 8.52.

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References and Notes

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