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Synthesis of Some New Aza Tricyclic Compounds with a Cyclopropane Ring *via* Photolysis of Dihydromayurone Oximes and the Related Compounds

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Oximation of dihydromayurone and 6,10,10-trimethyltricyclo[4.4.0.0^{1,3}]decan-4-one gives new isomeric oximes, respectively. The Beckman rearrangement of (*Z*)- or (*E*)-dihydromayurone oxime and (*Z*)- or (*E*)-6,10,10-trimethyltricyclo[4.4.0.0^{1,3}]decan-4-one oxime with polyphosphoric acid takes place prior to the *Z-E* equilibration of these isomers, respectively. Photolysis of the oximes gives two pairs of the isomeric lactams, 4-aza-8,12,12-trimethyltricyclo[6.4.0.0^{1,3}]dodecan-5-one, 5-aza-8,12,12-trimethyltricyclo[6.4.0.0^{1,3}]dodecan-4-one, 4-aza-7,11,11-trimethyltricyclo[5.4.0.0^{1,3}]undecan-5-one, and 5-aza-7,11,11-trimethyltricyclo[5.4.0.0^{1,3}]undecan-4-one. The reaction of either dihydromayurone or 6,10,10-trimethyltricyclo[4.4.0.0^{1,3}]decan-4-one with hydroxylamine-*O*-sulfonic acid in acetic acid affords only the lactam arising from the migration of the less substituted carbon.

Since the first study on the photo-Beckmann rearrangement of aromatic aldoximes by de Mayo,[1] a number of the related investigations have been reported. The mechanistic aspects of this intriguing and potentially useful photo chemical rearrangement have also been discussed for aromatic aldoximes,[2] and naphthalenone oxime,[3] styryl ketone oximes,[4] and alicyclic ketone oximes.[5–13] The formation of amides by photolysis of oximes is considered to take place *via* oxaziridine intermediates formed rapidly from the excited state oximes, which have been proved to be of a singlet state for the aromatic aldoximes[2] and the styryl ketone oxime rearrangement.[4]

In the photo-Beckmann rearrangement of the steroidal ketone oximes, we have recently reported[8,9] that the original configuration of C-α in the produced lactam with respect to the hydroxyimino group of the starting oxime was retained, irrespective of the configuration of the hydroxyimino group of the starting oxime.

We wish to report the photolysis and the Beckmann rearrangement of dihydromayurone oximes and 6,10,10-trimethyltricyclo[4.4.0.0^{1,3}]decan-4-one oximes, derived[14,15] both from a sesquiterpene thujopsene. We also report the reaction of the starting ketones (**1**) and (**4**) with hydroxylamine-*O*-sulfonic acid.[16,17] Considering that photolysis and the Beckmann rearrangement of an α,β-unsaturated ketone oxime are generally inferior to those of an alicyclic ketone oxime, we believe that the reactions of cyclopropyl ketone system which has a partial property of α,β-unsaturated ketone are important both from the synthetic and mechanistic points of view.

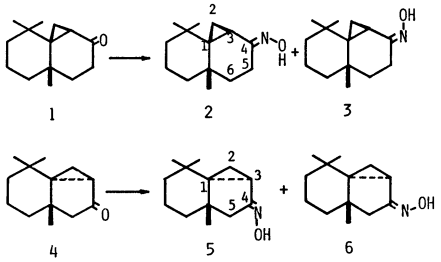
Results and Discussion

Preparation of Dihydromayurone Oximes (2), (3), and 6,10,10-Trimethyltricyclo[4.4.0.0^{1,3}]decan-4-one Oximes (5), (6). It was found that oximation of dihydromayurone[14] (**1**) gave a 2 : 1 mixture of new two isomeric oximes, which could be separated by preparative TLC into a less polar crystlline **2**, mp 136—137 °C and a more polar crystalline **3**, mp 160—161 °C. On the other hand, oximation of 6,10,10-trimethyltricyclo-[4.4.0.0^{1,3}]decan-4-one[15] (**4**) also afforded the two isomeric crystalline oximes **5**, mp 103—105 °C and **6**, mp 106—107 °C in the ratio of 1.3:1, which could be separated by TLC.

The configurations of **2**, **3**, **5**, and **6** were established both by the following ^{1}H NMR spectra and the Beckmann rearrangement.

Generally, hydrogens on an α-carbon atom to the oximino group are known to appear downfield[18] and especially, a *Z*-hydrogen disposed coplanar with a hydroximino hydroxyl group considerably downfield in the ^{1}H NMR spectrum.

In the ^{1}H NMR spectra of **2**, **3**, **5**, and **6**, the signals of C-5-H$_2$ of **2** and **5** appeared more downfield, and the signals of C-3-H of **2** and **5** appeared more upfield



Scheme 1.

Table 1. ^{1}H NMR spectra [δ, $CDCl_3$, TMS] of C-3-H and C-5-H$_2$ of the oximes (**2**), (**3**), (**5**), and (**6**)

Oxime	C-3-H(J/Hz)[a]	C-5-H$_2$(J/Hz)
2	1.90 (dd, J=5 and 10 Hz)	2.20—2.40 (m)
3	2.41 (dd, J=5 and 10 Hz)	2.10 (m)
5	2.03 (dd, J=4 and 8 Hz)	1.71 and 2.50 (AB-q, J=17 Hz)
6	2.56 (dd, J=4 and 8 Hz)	1.81 and 2.00 (AB-q, J=16 Hz)

a) This assignment was confirmed by the decoupling study with C-2-H$_2$.

than those of **3** and **6**, as shown in Table 1. These results indicated that **2**, **5** and **3**, **6** were assigned to *E*- and *Z*-configuration, respectively. These assignments were supported by the following Beckmann rearrangement.

Beckmann Rearrangement of the Oximes (2) and (3). Treatment of **2** with polyphosphoric acid[19] (PPA) at 90 °C for 10 min afforded the two new lactams (**7**), mp 156—161 °C, and (**8**), mp 118—120 °C, in 40 and 7% yields (by GLC analysis), respectively. On the other hand, the Beckmann rearrangement of **3** under the same conditions afforded **7** and **8** in 10 and 41% yields. The new lactams **7** and **8** were identified as 4-aza-8,12,12-trimethyltricyclo[6.4.0.0^{1,3}]dodecan-5-one and 5-aza-8,12,12-trimethyltricyclo[6.4.0.0^{1,3}]dodecan-4-one, respectively, on the ^{1}H NMR spectral ground.

In the spectrum of **7**, signals due to protons at C-3, C-6, and N atoms appeared as a double doublet at δ 2.57 (J=4 and 9 Hz), as a multiplet at δ 2.10, as a broad singlet at δ 6.62 (W_H=12 Hz), respectively. It is noteworthy that one proton signal was observed abnormally at down field as a double doublet at δ 2.91 (J=8, 12, and 12 Hz). Irradiation at δ 2.10 (C-6-H$_2$) collapsed the double double doublet at δ 2.91 into a double doublet (J=8 and 12 Hz), indicating the signal in question to be assigned to one proton at C-7. With an aim to clarify the structure of **7**, dihydromayurone (**1**) was treated with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane giving a lactone, 8,12,12-trimethyl-4-oxatricyclo-[6.4.0.0^{1,3}]dodecan-5-one (**9**). The ^{1}H NMR spectrum of **9** was similar to that of **7**; the signals of C-3-H, C-7-H, and C-6-H$_2$ appeared as a double doublet (δ 3.77, J=4 and 8 Hz), a double double doublet (δ 3.01, J=8, 12, and 12 Hz), and a multiplet (δ 2.30), respectively. While the C-7 proton of **9** appeared downfield by 0.1 ppm from the corresponding proton of **7**, and displayed the same splitting pattern, supporting the structure of **7** and **9**.

In the ^{1}H NMR spectrum of **8**, the signal due to N-proton was observed as a broad singlet at δ 7.18 (W_H=20 Hz). Moreover, the signal due to two C-6-protons appeared as two multiplets at δ 3.13 (1H) and 3.82 (1H). By addition of D_2O, the signal due to N-proton disappeared and the two multiplets were converted into a double double doublet and a double doublet centered at δ 3.82 (J=5, 12, and 14 Hz) and 3.13 (J=6 and 14 Hz), respectively. This also supports the structure of **8** as depicted in Scheme 2.

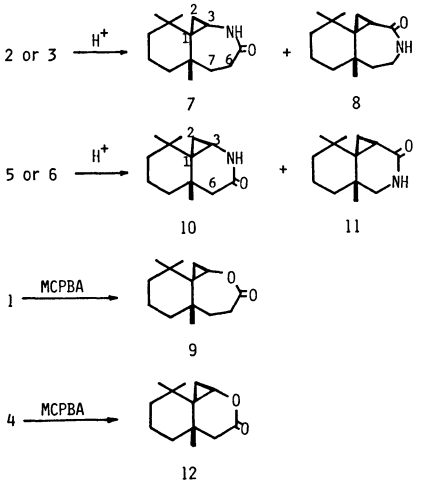
In the Beckmann rearrangement of oximes in general, it is well known[20] that the C–C bond oriented at the antiposition with respect to the hydroximino hydroxyl group migrates. Our results indicated that the equilibration between **2** and **3** took place to some extent prior to rearrangement under our experimental conditions. However, judging from the results, its rearrangement proceeded faster than the isomerization. These facts strongly suggested that the *E*- and *Z*-configurations were reasonably assigned to **2** and **3**, respectively.

Beckmann Rearrangement of the Oximes (5) and (6). Treatment of **5** with PPA at 90 °C for 5 min gave the two new lactams (**10**), mp 206—207 °C, and (**11**), mp 149—151 °C in 46 and 10% yields, respectively. On the other hand, the same treatment of **6** afforded **10** and **11** in 12 and 40% yields. On the basis of the ^{1}H NMR spectra, these lactams were assigned to the respective formulas, 4-aza-7,11,11-trimethyltricyclo[5.4.0.0^{1,3}]undecan-5-one and 5-aza-7,11,11-trimethyltricyclo[5.4.0.0^{1,3}]undecan-4-one, shown in Scheme 2. In the spectrum of **10**, signals due to protons at C-3, C-6, and N atoms appeared as a double doublet at δ 2.81 (J=5 and 10 Hz), as an AB-quartet at δ 1.80 and 2.12 (J=16 Hz) and as a broad singlet at δ 8.27 (W_H=16 Hz), respectively. Moreover, a new lactone, 7,11,11-trimethyl-4-oxatricyclo[5.4.0.0^{1,3}]-undecan-5-one (**12**) was prepared by treatment of **4** with MCPBA, and the structure of **10** was confirmed by the comparison with the spectra of **12**.

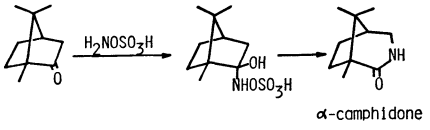
In the ^{1}H NMR spectrum of **11**, the signals of two C-6-protons appeared as a doublet at δ 2.91 (1H, J=13 Hz) and a double doublet at δ 2.48 (1H, J= 6 and 13 Hz). Addition of D_2O collapsed the double doublet at δ 2.48 into a doublet (J=13 Hz). The signal due to C-3-proton was not observed at downfield in the spectrum, again supporting the structure of **11** as indicated in Scheme 2.

These results confirmed the orientation of each hydroximino hydroxyl group of **5** and **6**.

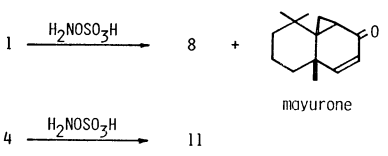
Reaction of the Ketones (1) and (4) with a Hydroxylamine-O-sulfonic Acid. It has been reported that treatment of ketone with hydroxylamine-*O*-sulfonic acid[16] produced lactam, and camphor was converted into only α-camphidone[17] which is produced from less substituted α-carbon. Since the migration in the Beckmann rearrangement usually occurs from the more substituted α-carbon, the above result suggests "unusual" Beckmann rearrangement. Then, we attempted the reaction of the cyclopropyl ketone systems **1** and **4**.



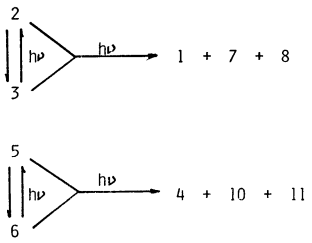
Scheme 2.



Scheme 3.



Scheme 4.



Scheme 5.

Treatment of **1** with hydroxylamine-*O*-sulfonic acid in acetic acid under reflux for 20 h gave **8** and mayurone in 33 and 24% yields, respectively. On the other hand, treatment of **4** under the same conditions afforded only **11** in 86% yield. These results indicated that the migration of less substituted α-carbon (C-5) took place predominantly (unusual Beckmann type).

Photolysis of Dihydromayurone Oximes (2) and (3). The photo-Beckmann rearrangement of **2** and **3** was carried out in methanol under nitrogen atmosphere at room temperature with a 15 W low pressure mercury lamp placed in the solution. Examination of the reaction by TLC indicated that a rapid photostationary equilibration between the *E*- and *Z*-forms took place, and, after 3 h, nearly equal amounts of *E*- and *Z*-forms were present in the solution. However, the photolysis for 20 h led to formation of several products, which were separated roughly into three fractions by column chromatography over silica gel. The least polar fraction consisted mainly of **1** in 40% yield, while the middle and the most polar fractions were found to contain **4** and **5** in the 10 and 13% yields, respectively. These products were identified by direct comparison with the spectra of the authentic samples.

The Photo-Beckmann Rearrangement of 5 and 6. The photo-Beckmann rearrangements of **5** and **6** were carried out under the same conditions as in the case of **2** and **3**. Examination of the reaction mixture after 5 h by TLC also revealed the presence of nearly equal amounts of *E*- and *Z*-forms in the solution. Further photolysis for 20 h resulted only in partial transformation of the oximes giving several products. Since further irradiation appeared to cause secondary photochemical decomposition of the initial products, the irradiation was stopped at this stage. The products were separated into four fractions by column chromatography over silica gel. The least polar fraction was found to be **4** in 24% yield by its spectra. The second least polar fraction (41%) consisted of a 1:1 mixture of the unreacted oximes. The third least and most polar fractions (3 and 5%) contained lactams **10** and **11**, respectively.

The results of the photolysis were summarized as follows. (i) The photo-Beckmann rearrangement of the conjugated cyclopropyl ketone oximes afforded the corresponding lactams. (ii) However, the yields of lactams were poor probably owing to the steric effect in the starting oximes and a property of a partial unsaturation of the cyclopropane ring. The major portion of products was the parent ketone arising from elimination of the nitrogen moiety of the intermidiary oxaziridines.

Experimental

All melting points were determined with a Shimadzu micro-apparatus. IR and ^1H NMR were determined with a Shimadzu IR-400 spectrometer and with a JEOL JNM-PMX-60 and/or a JEOL PS 100 high resolution spectrometer (solvent, chlorofrom-*d*; internal reference, tetramethylsilane), respectively. TLC and column chromatography were carried out on Wakogel B and on Cica Silica gel. GLC was carried out on a Shimadzu 4BM (column; 1.5% SE-30, 1.5 m). Elemental analysis were determined with a Hitachi CHN Analyzer. Mass spectra were taken by the staff of the Faculty of Pharmaceutical Science, Hokkaido University, with a RMU-6E spectrometer.

Dihydromayurone Oximes (2) and (3). Dihydromayurone (**1**) (2.06 g) in 90% aq ethanol (150 ml) was refluxed for 2 h with hydroxylamine hydrochloride (1.00 g) and sodium acetate (1.50 g). After removal of solvent, the reaction mixture was mixed with ether. The ether layer was washed with water, dried (Na_2SO_4), and evaporated to leave crystals, which were found to consist of two isomeric compounds by the ^1H NMR and TLC. These compounds were separated by repeated preparative TLC with a 4:1 mixture of benzene and acetone into **2** (1.04 g) and **3** (0.50 g).

Oxime **2**, mp 136—137 °C (from ethanol); MS, *m/e* 221 (M^+, 18%), 204 ($M^+ - OH$); IR ν_{max} (KBr) 3250 (-OH), 3020 (cyclopropane), and 1650 cm^{-1} (-C=N-); ^1H NMR, δ 1.90 (dd, 1H, $J=5$ and 10 Hz, C-3-H), 2.20—2.40 (m, 2H, C-5-H_2), 0.64, 1.14 and 1.19 each (s, 3H, -CH_3); Found: C, 75.76; H, 10.61; N, 6.20%. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33%.

Oxime **3**, mp 160—161 °C (from ethanol); MS, *m/e* 221 (M^+, 22%), 204 ($M^+ - OH$, 7); IR, ν_{max} (KBr) 3250 (-OH), 3020 (cyclopropane), and 1650 cm^{-1} (-C=N-); ^1H NMR, δ 2.41 (dd, 1H, $J=5$ and 10 Hz, C-3-H), 2.10 (m, 2H, C-5-H_2), 0.66, 1.10, and 1.16 each (s, 3H, -CH_3), Found: C, 75.88; H, 10.58; N, 6.32%. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33%.

6,10,10-Trimethyltricyclo[4.4.0.0^{1,3}]decan-4-one Oximes (5) and (6). The starting ketone (**4**) (0.96 g) in 90% aq ethanol (50 ml) was refluxed for 1 h with hydroxylamine hydrochloride (0.50 g) and sodium acetate (0.54 g). After removal of solvent, the reaction mixture was mixed with ether. The ether solution was washed with water, dried (Na_2SO_4), and evaporated to leave crystals, which were separated by repeated preparative TLC with a 5:1 mixture of benzene and acetone to afford **5** (460 mg) and **6** (350 mg).

Oxime **5**, when recrystallized from ethanol, had mp 103—105 °C; MS, *m/e* 207 (M^+, 17%), 190 ($M^+ - OH$, 25); IR, ν_{max} (KBr) 3280 (-OH), 1650 cm^{-1} (-C=N-); ^1H NMR, δ 2.03 (dd, 1H, $J=4$ and 8 Hz, C-3-H), 2.50 and 1.71 (AB-q, $J=17$ Hz, C-5-H_2), 0.60, 1.06, and 1.16 each (s, 3H, -CH_3); Found: C, 75.25; H, 10.05; N, 7.01%. Calcd for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76%.

Oxime **6**, when recrystallized from ethanol, had mp 206—207 °C; MS, *m/e* 207 (M^+, 14%), 190 ($M^+ - OH$, 28); IR; ν_{max} (KBr), 3300 (OH), and 1650 cm^{-1} (-C=N-); ^1H NMR, δ 2.56 (dd, 1H, $J=4$ and 8 Hz, C-3-H), 1.81 and 2.00 (AB-

q, 2H, $J=16$ Hz, C-5-H_2), 0.63, 1.06, and 1.14 each (s, 1H, -CH_3); Found: C, 75.31; H, 10.24; N, 7.22%. Calcd for $C_{13}H_{21}NO$: 75.31; H, 10.21; N, 6.76%.

Rearrangement of ***2*** *with PPA.* **2** (400 mg) was added into polyphosphoric acid (20 g) at 90 °C, stirred with glass stick for 10 min, and cooled. To the reaction mixture was added 10% aq sodium carbonate and ether. The ether solution left oily residue, which was separated by column chromatography over silica gel to afford lactam **7** (123 mg) and **8** (25 mg).

Lactam **7**, mp 156—160 °C (from hexane); MS, *m/e* 221 (M^+, 19%); IR, ν_{max} (KBr) 3010 (cyclopropane), 3200 (-NH), and 1670 cm^{-1} (carbonyl); ^1H NMR, δ 2.57 (dd, 1H, $J=4$ and 9 Hz, C-3-H), 2.10 (m, 2H, C-6-H_2), 2.91 (ddd, 1H, $J=8$, 12, and 12 Hz, C-7-H), 6.62 (broad s, 1H, $W_H=12$ Hz, NH), 0.56, 0.85, and 1.18 each (s, 3H, -CH_3); Found: C, 75.68; H, 10.58; N, 6.18%. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33%.

Lactam **8**, mp 118—120 °C (from hexane); MS, *m/e* 221 (M^+, 24%); IR, ν_{max} (KBr) 3200 (-NH) and 1670 cm^{-1} (carbonyl); ^1H NMR, δ 3.13 and 3.82 each (m, 1H, C-6-H), 7.18 (broad s, 1H, $W_H=20$ Hz), 0.63, 0.83, and 1.13 each (s, 3H, -CH_3); Found C, 75.69; H, 10.55; N, 6.06%. Calcd for $C_{14}H_{23}NO$: C, 75.97; H, 10.47; N, 6.33%.

Rearrangement of ***3*** *with PPA.* **3** (400 mg) was added into polyphosphoric acid (20 g) at 90 °C and stirred with glass stick for 10 min. Usual work-up afforded **7** (400 mg) and **8** (164 mg).

*8,12,12-Trimethyl-4-oxatricyclo[6.4.0.0^{1,3}]dodecan-5-one (**9**).* **1** (300 mg) and *m*-chloroperbenzoic acid (700 mg) in dichloromethane (20 ml) were refluxed for 20 h, and then cooled. After addition of 10% aq sodium carbonate, the mixture was extracted with dichloromethane. The dichloromethane solution was washed with water and dried (Na_2SO_4). The residue, obtained by removal of solvent by column chromatography over silica gel to afford crystals (154 mg), which on recrystallization from hexane gave lactone **9**, mp 120—122 °C; MS, *m/e* 222 (M^+, 0.3%); IR, ν_{max} (KBr) 1750 and 1270 cm^{-1} (lactone); ^1H NMR δ 3.77 (dd, 1H, $J=4$ and 8 Hz, C-3-H), 2.30 (m, 2H, C-6-H_2), 3.01, (ddd, 1H, $J=8$, 12, and 12 Hz, C-7-H), 0.59, 0.88, and 1.19 each (s, 3H, -CH_3); Found: C, 75.68; H, 9.81%. Calcd for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97%.

Rearrangement of ***5*** *with PPA.* **5** (200 mg) was added into warm polyphosphoric acid (10 g) at 100 °C and stirred with grass stick for 10 min, and cooled. To the reaction mixture was added 10% aq sodium carbonate, and ether. The ether sulution was washed with water, and dried (Na_2SO_4); the residue obtained by removal of solvent was separated by column chromatography over silica gel to give two lactams **10** (92 mg) and **11** (20 mg).

Lactam **10**, when recrystallized from hexane, had mp 206—207 °C; MS, *m/e* 207 (M^+, 25%); IR, ν_{max} (KBr) 3180 (NH) and 1680 cm^{-1} (carbonyl); ^1H NMR, δ 2.81 (dd, 1H, $J=5$ and 10 Hz, C-3-H), 1.80 and 2.12 (AB-q, $J=16$ Hz, C-6-H_2), 8.27 (broad s, 1H, $W_H=16$ Hz, NH), 0.59, 1.07, and 1.22 each (s, 3H, -CH_3); Found: C, 74.96; H, 9.91; N, 6.69%. Calcd for $C_{13}H_{21}NO$: C, 75.30; H, 10.21; N. 6.76%.

Lactam **11**, when recrystallized from hexane, had mp 149—151 °C; MS, *m/e* 207 (M^+, 25%); IR, ν_{max} (KBr) 3330 (NH), and 1670 cm^{-1} (carbonyl); ^1H NMR, δ 2.91 (d, 1H, $J=13$ Hz, C-6-H) and 2.48 (dd, 1H, $J=6$ and 13 Hz, C-6-H), 7.35 (broad s, 1H, $W_H=8$ Hz, NH), 0.62, 1.55, and 1.55 each (s, 3H, -CH_3); Found: C, 75.10; H, 10.20; N, 6.54%. Calcd for $C_{13}H_{21}NO$: C, 75.31; H, 10.21; N, 6.76%.

Rearrangement of ***6*** *with PPA.* **6** (200 mg) was converted into lactams **10** (23 mg) and **11** (80 mg) under the same conditions with rearrangement of **5**.

*7,11,11-Trimethyl-4-oxatricyclo[5.4.0.0^{1,3}]undecan-5-one (**12**)* **4** (220 mg) and *m*-chloroperbenzoic acid (700 mg) in dichloromethane (20 ml) were refluxed for 20 h. After being cooled, the reaction mixture was washed with 10% aq sodium carbonate and water, dried (Na_2SO_4), and evaporated to leave oily residue, which was purified by column chromatography over silica gel to yield lactone **12** (150 mg) in pure state.

Lactone **12**, recrystallization from hexane, mp 129—131 °C; MS, *m/e* 208 (M^+, 0.3%); IR, ν_{max} (KBr) 1740 and 1240 cm^{-1} (lactone); ^1H NMR, δ 4.13 (dd, 1H, $J=4$ and 8 Hz, C-3-H), 1.98 and 2.22 (AB-q, 2H, $J=17$ Hz, C-6-H_2), 0.61, 1.05, and 1.21 each (s, 3H, -CH_3); Found: C, 74.75; H. 9.63%. Calcd for $C_{13}H_{20}O_2$; C, 74.96; H, 9.68%.

Reaction of ***1*** *with Hydroxylamine-O-sulfonic Acid.* **1** (412 mg) and hydroxylamine-*O*-sulfonic acid (452 mg) in acetic acid (5 ml) were refluxed for 20 h under nitrogen atmosphere. After being cooled, to the reaction mixture was added 10% aq sodium hydroxide (20 ml) and ether. The ether layer was washed with water, and dried (Na_2SO_4). The products were separated by column chromatography over silica gel, using benzene, ether and acetone as solvent. Elution with 2:1 mixture of benzene and ether gave a single crystal (100 mg), which was identified with authentic mayurone. On the other hand, elution with 1:1 mixture of ether and acetone afforded a single crystal **8** (140 mg).

Reaction of ***4*** *with Hydroxylamine-O-sulfonic Acid.* **4** (190 mg) and hydroxylamine-*O*-sulfonic acid (170 mg) in acetic acid (3 ml) were refluxed for 20 h. After being cooled, to the reaction mixture was added 10% aq sodium hydroxide and ether. The ether layer was washed with water and dried (Na_2SO_4). Removal of solvent gave a crystal (176 mg), which was identified with **11**.

Photolysis of ***2*** *and* ***3***. A 2:1 mixture of **2** and **3** (1.50 g) in methanol (400 ml) was irradiated for 20 h with 15 W low pressure arc Hg lamp, while nitrogen was slowly bubbled through the solution. Removal of methanol left oily residue, which was separated by column chromatography over silica gel to give **1** (600 mg, from 2:1 mixture of benzene and ether), **7** (150 mg, from ether), and **8** (200 mg, from 1:1 mixture of ether and acetone). They were identical with authentic compounds, respectively.

Photolysis of ***5*** *and* ***6***. A 1.3:1 mixture of **5** and **6** (2.0 g) in methanol (400 ml) was irradiated for 20 h with 15 W low pressure arc Hg lamp, while nitrogen was slowly bubbled through the solution. The oily residue, obtained removal of methanol, was separated by column chromatography over silica gel to afford **4** (447 mg, from 2:1 mixture of benzene and ether), **5** and **6** (825 mg, from 1:1 mixture of benzene and ether), **10** (67 mg, from ether) and **11** (100 mg, from 1:1 mixture of ether and acetone), which were identical with the respective authentic compounds.

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