(Nujol) 3375, 3315, 3250, 1762, and 1725 cm^{-1}; nmr (CD$_3$OD) δ 1.4 (s, 3 H, C-CH$_3$), 1.7 (m, 4 H, CCH$_2$CH$_2$-), 3.5 (t, 2 H, OCH$_2$-); homogenous in solvent systems B (0.44) and C (0.54). *Anal.* (C$_7$H$_{12}$N$_2$O$_3$) C, H, N.

5-(3-Chloropropyl)-5-methylhydantoin (2). To 5 g (0.029 mol) of **1** and 2.52 g (0.032 mol) of pyridine, cooled to 0° and protected from moisture, was added 2.19 ml (0.03 mol) of thionyl chloride in 10 ml of CHCl$_3$ over a 1-hr period. The solution was stirred for an additional 3 hr, at which time the reaction had warmed to room temperature. The temperature was then raised to 55° for 30 min. After removal of the chloroform *in vacuo* the resulting viscous oil was dissolved in 10 ml of H$_2$O and extracted with ether (4 × 20 ml). The ether was dried over MgSO$_4$ and evaporated *in vacuo* to yield 4 g of solid (73%). An analytical sample was obtained by crystallization from benzene: mp 127–129°; ir (KBr) 3300–3100 (br), 1750, 1700, and 1425 cm^{-1}; nmr (CD$_3$OD) δ 1.4 (s, 3 H, CCH$_3$), 1.8 (m, 4 H, CCH$_2$CH$_2$-), 3.5 (t, 2 H, ClCH$_2$-); homogenous in solvents systems B (0.60) and E (0.36). *Anal.* (C$_7$H$_{11}$ClN$_2$O$_2$) C, H, Cl, N.

5-Methyl-1,5-trimethylenehydantoin (3). A 500-ml Parr hydrogenation bottle was charged with 1.7 g (0.009 mol) of **2**, 8.6 g (0.09 mol) of ammonium carbonate, and 20 ml of 30% aqueous NH$_3$. The bottle was securely stoppered and stirred for 16 hr at a temperature of 40°. Solvent was then removed *in vacuo* and the resulting oil was dissolved in dilute HCl and applied to a strong cation exchange resin (Amberlite IRC 120, H$^+$ form). The column was washed with 4 *N* NH$_4$OH and the eluent was taken to dryness. The white solid, 0.68 g (50%), was crystallized from H$_2$O to give an analytical sample: mp 129–131°; ir (KBr) 3175, 3060, 1745, 1700–1675, and 1375 cm^{-1}; nmr (CD$_3$OD) δ 1.4 (s, 3 H, CCH$_3$), 2.0 (m, 4 H, CCH$_2$CH$_2$C), 3.4 (m, 2 H, NCH$_2$), 4.9 (s, 1 H, NH); homogenous in solvent systems A (0.64), B (0.58), and C (0.59). *Anal.* (C$_7$H$_{10}$N$_2$O$_2$) C, H, N.

Compound **3** was obtained in 80% yield by refluxing **2** with 2 mol of NaOMe for 3 hr and then neutralizing and extracting the cyclized product from an aqueous solution with ether.

2-Methylproline (4). A glass liner bottle for a high-pressure reaction apparatus was charged with 2 g (0.01 mol) of **2**, 6.3 g (0.02 mol) of Ba(OH)$_2$·8H$_2$O, and 50 ml of H$_2$O. The solution was shaken for 30 min at 160° and then allowed to slowly return to room temperature. The pH was adjusted to 2 with 6 *N* H$_2$SO$_4$ and after filtering the BaSO$_4$ the filtrate was applied to a strong cation exchange resin (Amberlite IRC 120, H$^+$ cycle). Elution with 4 *N* NH$_4$OH and evaporation of solvent gave 1.2 g (90%) of a white solid, mp 252–258°. Crystallization from MeOH-Et$_2$O gave an analytical sample: mp 263–264.5°; ir (KBr) 3450, 3200, and 1600 cm^{-1}; nmr (CD$_3$OD) δ 1.6 (s, 3 H, CCH$_3$), 1.9 (m, 4 H, CCH$_2$CH$_2$C), 3.3 (m, 2 H, -NCH$_2$); homogenous in solvent systems A (0.29), B (0.09), and C (0.14). *Anal.* (C$_6$H$_{11}$NO$_2$) C, H, N.

5-Methyl-5-(3-nitropropyl)hydantoin (5). The procedure and equipment were the same as for **1**. The quantities used were 30 g (0.23 mol) of 5-nitro-2-pentanone, 96 g (1 mol) of ammonium carbonate, 12.25 g (0.25 mol) of sodium cyanide, and 450 ml of 60% EtOH. Work-up gave a 20-g (43%) crude yield of **5**. Two crystallizations from absolute EtOH gave an analytical sample: mp 125–127°; ir (KBr) 3100 (br), 1750, 1700, and 1545 and 1385 cm^{-1} (NO$_2$); nmr (DMSO-d_6) δ 1.28 (s, 3 H, CH$_3$), 1.7 (m, 4 H, CCH$_2$CH$_2$C), 4.6 (t, 2 H, NCH$_2$), 8.0 (s, 1 H, NH), and 10.4 (s, 1 H, NH), homogenous in solvent systems A (0.70), B (0.60). *Anal.* (C$_7$H$_{11}$N$_3$O$_4$) C, H, N.

Reduction of 5-Methyl-5-(3-nitropropyl)hydantoin (5). A 500-ml Parr hydrogenation bottle was charged with 4 g (0.02 mol) of **5**, 0.25 g of platinum oxide (Adams catalyst), and 75 ml of anhydrous methanol. The solution was shaken for 18 hr at 45 psi and room temperature. Catalyst was removed by filtration and the methanol was evaporated *in vacuo*. The resulting white solid was crystallized from a minimum amount of hot methanol to give 2.45 g (72%) of 5-(3-aminopropyl)-5-methylhydantoin (**7**), mp 171–174°. Recrystallization gave an analytical sample, mp 175–177°. The filtrate from the first crystallization was reduced in volume and the precipitate **6** collected, 0.32 g (9%), mp 225–227°. Recrystallization of **6** from methanol gave an analytical sample, mp 235–236°. The elemental analysis and molecular weight of **6** and **7** were identical. A reduction time of 2 hr gave 60% of **6** and none of **7**. The analytical data for **6** and **7** follow. **6** had mp 235–236°; ir (KBr) 3460, 3365, 3285, 3190, 1670, 1590, and 1230 cm^{-1}; nmr (DMSO-d_6) δ 1.3 (s, 3 H, CCH$_3$), 1.8 (m, 4 H, -CCH$_2$CH$_2$C), 3.1 (m, 2 H, NCH$_2$-), 5.4 (s, 2 H, NH$_2$), 6.1 (s, 1 H, NH), 7.3 (s, 1 H, NH); mass spectrum molecular ion at *m/e* 171; homogeneous in solvent systems A (0.50), B (0.30), C (0.35). *Anal.* (C$_7$H$_{13}$N$_3$O$_2$) C, H, N. **7** had mp 175–177°; ir (KBr) 3250, 1575 (br), 1390 cm^{-1}; nmr (DMSO-d_6) δ 1.2 (s, 3 H, CCH$_3$), 1.5 (m, 4 H, CCH$_2$CH$_2$C), 2.5 (t, 2 H, NCH$_2$), 4.1 (br, 3 H, NH$_3$); mass spectrum molecular ion at *m/e* 171; homogenous in solvent systems A (0.42), B (0.14), C (0.12). *Anal.* (C$_7$H$_{13}$N$_3$O$_2$) C, H, N.

2-Methylornithine Sulfate (8). The hydrolysis procedure was the same as described for 2-methylproline (**4**). The quantities for a typical hydrolysis were 1 g (0.006 mol) of **6** or **7**, 3.78 g (0.012 mol) of Ba(OH)$_2$·8H$_2$O, and 50 ml of H$_2$O. The pH of the hydrolysis mixture was adjusted to 1.7 with H$_2$SO$_4$ and the BaSO$_4$ was removed by filtration and washed with hot H$_2$O. The combined filtrates were adjusted to pH 6.5 with saturated Ba(OH)$_2$ to remove excess H$_2$SO$_4$. Again the BaSO$_4$ was removed by filtration and the combined filtrates were evaporated *in vacuo*. The oily residue was redissolved in hot H$_2$O and crystallization was facilitated with absolute EtOH and 3 ml of dilute HCl to yield 0.73 g (50%) of product, mp 212–215°. Recrystallization gave an analytical sample: mp 216.5–217.5°; ir (KBr) 3300–2500, 1725, 1580, and 1325 cm^{-1}; nmr (D$_2$O) δ 1.6 (s, 3 H, -CCH$_3$), 1.95 (m, 4 H, -CCH$_2$CH$_2$C), 3.1 (t, 2 H, NCH$_2$); homogenous in solvent systems A (0.18) and C (0.05). *Anal.* (C$_6$H$_{16}$N$_2$O$_6$S) C, H, N, S.

Registry No. 1, 42856-68-8; **2**, 42856-69-9; **3**, 42856-70-2; **4**, 42856-71-3; **5**, 42856-72-4; **6**, 42856-73-5; **7**, 42856-74-6; **8** sulfate, 42856-75-7; 5-hydroxy-2-pentanone, 1071-73-4; 5-nitro-2-pentanone, 22020-87-7.

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(12) Satisfactory analytical data (±0.4%) were reported for compounds **1–8**.

Photoinduced Addition of Isopropyl Alcohol to α,β-Unsaturated Lactones[1]

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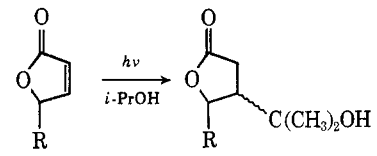
Photoinduced addition of isopropyl alcohol to the double bond adjacent to a carbonyl group has been reported of several ketones[2] and a lactone.[3] The product has been invariably found to be a β adduct. No quantitative study has been made, however, except for the case of 2-cyclopentenone,[2a] where the quantum yield for the photoinduced addition was merely estimated from disappearance of 2-cyclopentenone in dilute solution (0.01 *M*). In the present experiment, the direct excitation of α,β-unsaturated γ-lactones in isopropyl alcohol was found to afford the corresponding adducts with such high quantum yields that the reaction can be used for large-scale preparation.

When 2(5*H*)-furanone (**1**) in isopropyl alcohol was internally irradiated with a 30-W low-pressure mercury lamp, a single product was obtained after distillation of the



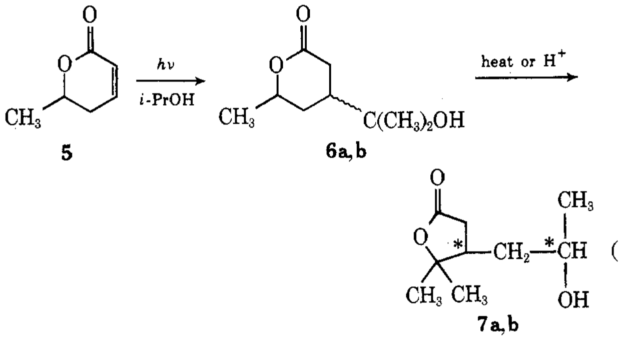
1, R = H
3, R = CH₃
2, R = H
4, R = CH₃

(1)

reaction mixture under reduced pressure. The product was identified as **2**, a photoadduct between **1** and isopropyl alcohol. Under irradiation for a few hours, 0.05 mol of **1** was transformed into **2** in 90% yield. The same type of reaction product (**4**) was obtained also on the irradiation of 5-methyl-2(5*H*)-furanone (**3**) under similar conditions.

The quantum yield for the formation of **2** from **1** was measured under the irradiation of deaerated samples with 248-nm light. The quantum yields varied with the concentration of **1** and exceeded unity in all cases. The quantum yield in Table I indicates that the reaction involves a free-radical chain, which may be initiated by the formation of a ketyl radical as a consequence of hydrogen abstraction of the photoexcited carbonyl group from isopropyl alcohol. This is analogous to the case of cyclopentenone.[2] The free-radical chain mechanism is further supported by the fact that the same addition products as above were obtained also on the thermal decomposition (75°, 45 min) of benzoyl peroxide (9×10^{-3} *M*) in isopropyl alcohol solutions of **1** and **3**.

In order to investigate whether the photoinduced addition takes place also with six-membered lactones, the isopropyl alcohol solution of 5,6-dihydro-6-methyl-2*H*-pyran-2-one (**5**) was irradiated. The rate of photochemical conversion of **5** was so low that **5** was hardly consumed even after an irradiation period in which **1** was completely transformed into **2**. At least a ten times longer irradiation period was required to obtain the photoadducts. The photoadducts were so unstable that only one of the stereoisomers (**6a**) was directly isolated (yield 16%); the formation of the other isomer (**6b**) was indicated on the basis of the fact that γ-lactone **7b** was isolated (yield 36%) as a final product. The direct product **6a** also was easily converted into the corresponding γ-lactone (**7a**) in the presence of acid catalyst.



5
6a,b
7a,b

(2)

The same addition products were easily obtained on the thermal decomposition of benzoyl peroxide in isopropyl alcohol solution of **5** (Table II). In comparison with the thermal reaction, the extremely small yield of the photoadduct of **5** indicates that the quantum yield for hydrogen abstraction of **5** is much less than that for either **1** or **3**.

Experimental Section

Materials. 2(5*H*)-Furanone was prepared as described previously.[4] Thiele, Tischbein, and Lossows' procedure[5] was used to prepare 5-methyl-2(5*H*)-furanone. 5,6-Dihydro-6-methyl-2*H*-pyran-2-one was synthesized according to the method of Kuhn and Jerchel.[6]

Table I
Quantum Yield of 2 under Irradiation of 1 with 248-nm Light

[1] (10^{-1} *M*)	1.40	2.62	5.49	7.96
Quantum yield	30	11	5.7	2.8

Table II
Yield of the Isopropyl Alcohol Adduct of α,β-Unsaturated Lactones

Compd	Photoinduced reaction[a]	Thermal reaction induced by benzoyl peroxide[b]
1	52	59
3	35	27
5	0	12

[a] Irradiation time, 10 min. [b] Reaction time, 45 min.

Irradiation in Preparative Scale. An isopropyl alcohol solution (100–300 ml) of α,β-unsaturated lactone (0.04–0.18 *M*) was internally irradiated under a nitrogen stream with a 30-W low-pressure mercury immersion lamp (Riko-Sha UVL-303Q).

Determination of Quantum Yields. The light source was a Ushio 500-W super-pressure mercury arc lamp (USH-500D). The 248-nm band was isolated with a Hitachi Model EPU-2A spectrometer (quartz prism, half-height width 4 mμ). The beam of the monochromatic light was divided into two portions by the use of an optically flat quartz plate tilted by 45° with respect to the light beam. The transmitted light (3.6×10^{14} quanta/sec) was used to irradiate the sample, and an actinometer cell, containing ferrioxalate solution, was irradiated by the light reflected perpendicular to the transmitted light (approximately 10% of the intensity of the transmitted light). Pure isopropyl alcohol for fluorescence spectroscopy was used to prepare sample solutions, which were degassed by the freeze–thaw technique and were successively transferred into a cylindrical cell (20 × 10 mm) *in vacuo* (less than 10^{-4} mm). Irradiations were carried out at a constant temperature (30.0 ± 0.1°) to less than 5% conversion. The amounts of adducts were determined against an internal reference (benzophenone) by the use of a Shimadzu GC-2C chromatograph equipped with a thermal conductivity detector. Analysis was performed with a column (2.25 m × 3 mm) packed with 10% polyphenyl ether (five rings) on Chamelite CS 60/80. The column temperature was 180°, and the carrier gas was hydrogen.

Determination of Relative Reactivity between the Unsaturated Lactones. Each set of sample tubes containing the appropriate solution ($\sim 10^{-1}$ *M*) was either externally irradiated or kept at 75°, depending on the purpose of the experiment, for a given period of time. Then the amount of isopropyl alcohol adduct in each sample tube was determined by measuring the area under the peak of the corresponding proton signals.

4-(1′-Hydroxy-1′-methylethyl)-4,5-dihydro-2(3*H*)-furanone (2). Distillation of the irradiated sample under reduced pressure afforded pure **2** as a viscous liquid: bp 139–140° (3 mm); ir (neat) 3400 (broad), 1783 (s), 1775 (shoulder), 1180 cm^{-1} (broad); nmr (in benzene) δ 0.96 (s, 6 H), 1.8–2.7 (m, 3 H), 2.92 (s, 1 H), 2.8–4.4 (m, 2 H). The nmr signals of methylene protons adjacent to the ethereal oxygen atom of **2** in KOD-D_2O solution split into an octet, which indicates that the geminal protons are in nonequivalent electromagnetic circumstances ($\Delta\nu_{AB} = 9.8$, $J_{AB} = 11.0$ Hz) and both of the protons are coupled to a methine proton ($J_{AC} = 5.5$ and $J_{BC} = 5.0$ Hz). On the basis of this evidence, β-adduct structure was assigned to **2**. Treatment of **2** with 3,5-dinitrobenzoyl chloride in pyridine at 70° afforded the 3,5-dinitrobenzoate in 88% yield: mp 135–136° from methanol; ir (KBr) 1775 (shoulder), 1765 (s), 1717 (s), 1545 (s), 1347 (s), 1295 (s), 1178 (s), 1121 cm^{-1} (s); nmr ($CDCl_3$) δ 1.78 (s, 6 H), 2.5–3.5 (m, 3 H), 4.4–4.7 (m, 2 H), 9.0–9.3 (m, 3 H).

Anal. Calcd for $C_{14}H_{14}O_8N_2$: C, 49.71; H, 4.17; N, 8.25. Found: C, 49.89; H, 4.23; N, 8.26.

4-(1′-Hydroxy-1′-methylethyl)-5-methyl-4,5-dihydro-2(3*H*)-furanone (4). The sample was easily purified by distillation under reduced pressure: bp 144–145° (5 mm); ir (neat) 3500 (broad), 1755 (s), 1777 (shoulder), 1190 cm^{-1} (s); nmr (in benzene) δ 0.99 (s, 6 H), 1.19 (d, $J = 6.0$ Hz, 3 H), 1.4–2.7 (m, 3 H), 2.80 (s, 1 H), 4.55 (dq, $J_1 = J_2 = 6.0$ Hz, 1 H). The nmr signals of the methine proton adjacent to the oxygen atom of **4** in KOD–D_2O solution was found to be a doublet (J_1 = 1.8 Hz) of quartets (J_2 = 6.5 Hz). As a result of a decoupling experiment, J_1 was found to correspond to the vicinal coupling between the two methine groups in agreement with the assignment of β-adduct structure to **4**. Analogously to the case of **2**, the 3,5-dinitrobenzoate of **4** was obtained in 83% yield: mp 140–143° from methanol; ir (KBr) 1781 (s), 1721 (s), 1550 (s), 1347 (s), 1292 (s), 1179 (s), 1120 cm^{-1} (m); nmr ($CDCl_3$) δ 1.51 (d, 3 H), 1.73 (s, 6 H), 2.3–3.1 (m, 3 H), 4.80 (dq, J_1 = 6.6, J_2 = 2.8 Hz, 1 H), 9.0–9.3 (m, 3 H).

Anal. Calcd for $C_{15}H_{16}O_8N_2$: C, 51.14; H, 4.58; N, 7.95. Found: C, 51.12; H, 4.57; N, 8.09.

Isopropyl Alcohol Adducts of 5,6-Dihydro-6-methyl-2*H*-pyran-2-one. By the use of silica gel chromatography (eluent, benzene–ethyl acetate mixture in 1:1 ratio by v/v), two adducts were separated from the reaction mixture, **7b** (yield 36%) and **6a** (yield 16%). On the basis of both the spectroscopic and chemical evidences described below, **6a** and **7b** were concluded to be δ- and γ-lactone, respectively.

A. γ-Lactone 7b was a viscous liquid: ir (neat) 3440 (broad), 1760 (broad), 1273 cm^{-1} (broad); nmr (in benzene) δ 0.95 (s, 3 H), 1.22 (s, 3 H), 1.10 (d, J = 6.2 Hz, 3 H), 0.8–2.8 (m, 5 H), 2.99 (s, 1 H), 3.2–3.8 (m, 1 H); nmr ($CDCl_3$) δ 1.24 (d, J = 6.2 Hz, 3 H), 1.25 (s, 3 H), 1.45 (s, 3 H), 1.3–1.7 (m, 2 H), 1.7–3.0 (m, 3 H), 2.74 (s, 1 H), 3.5–4.1 (m, 1 H). The frequency of the carbonyl absorption band corresponds to those of saturated γ-lactones. As to the nmr spectra, we observe two singlet signals which correspond to three protons, respectively: the difference in chemical shifts between the two signals is as large as 0.2 ppm in both benzene and deuteriochloroform. It is suggested then that there are two highly nonequivalent methyl groups. In addition, the benzene-induced shifts for these singlets are much larger than that for the doublet (1.10 ppm in benzene) which is assigned to the methyl protons coupled to an adjacent methine proton. These facts are in good agreement with the proposed structure **7b**, but not with **6b**. Finally, the hydroxyl proton signal of **7b** splits into a doublet (J = 4.9 Hz), when the acetone solution is cooled down below −10°. Therefore, a secondary hydroxyl group must be involved in **7b**. The structure of **7b** is thus deduced. The corresponding 3,5-dinitrobenzoate was obtained by the usual method in 93% yield: mp 180–181° from methanol; ir (KBr) 1767 (s), 1756 (shoulder), 1726 (s), 1544 (s), 1347 (s), 1279 (s), 1173 (m), 1133 cm^{-1} (m); nmr ($CDCl_3$) δ 1.31 (s, 3 H), 1.48 (s, 3 H), 1.51 (d, J = 6.0 Hz, 3 H), 1.2–2.9 (m, 5 H), 5.0–5.5 (m, 1 H), 9.0–9.3 (m, 3 H).

Anal. Calcd for $C_{16}H_{18}O_8N_2$: C, 52.47; H, 4.95; N, 7.65. Found: C, 52.52; H, 4.94; N, 7.45.

B. δ-Lactone 6a was a viscous liquid: ir (neat) 3510 (broad), 1729 (s), 1254 cm^{-1} (broad); nmr (in benzene) δ 0.98 (s, 6 H), 1.09 (d, J = 6.2 Hz, 3 H), 0.9–2.5 (m, 5 H), 2.46 (s, 1 H), 3.5–4.2 (m, 1 H). The proton signals of **6a** in $CDCl_3$ gradually disappear and new sets of signals arise in return. Then a benzene solution of **6a** was prepared and a very small amount of dry hydrogen chloride was bubbled into the solution. This treatment completed the transformation from **6a** into the new compound **7a**, which was easily recovered by purging the solvent with a nitrogen stream.

C. γ-Lactone 7a was recrystallized from *n*-hexane–benzene mixture: mp 122.5–123.5°; ir (KBr) 3250 (shoulder), 3400 (broad), 1761 (s), 1747 (shoulder), 1275 (m), 1262 (s), 1122 (s), 1103 cm^{-1} (s); nmr ($CDCl_3$) δ 1.23 (d, J = 6.3 Hz, 3 H), 1.25 (s, 3 H), 1.45 (s, 3 H), 1.3–1.7 (m, 2 H), 1.7–2.9 (m, 3 H), 2.68 (s, 1 H), 3.38 (tq, $J_1 = J_2$ = 6.3 Hz, 1 H). The structure of multiplets with a pair of prominent peaks around 2.5 ppm is clearly different from the corresponding multiplets of **7b** in which a single, sharp peak is observed at 2.5 ppm. The hydroxyl proton signal of **7a** also splits into a doublet (J = 4.8 Hz) when the acetone solution is cooled down. In vpc analyses, there is a small but clear difference in retention time between **7a** and **7b** so that a pair of slightly overlapping peaks are observed when both of the compounds are injected into the column at the same time.

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.88; H, 9.66.

Registry No. 1, 497-23-4; **2**, 42867-48-1; **2 3,5-dinitrobenzoate,** 42867-49-2; **3**, 591-11-7; **4**, 42867-50-5; **4 3,5-dinitrobenzoate,** 42867-51-6; **5**, 108-54-3; **6a**, 42867-52-7; **6b**, 42867-53-8; **7a**, 42867-54-9; **7b**, 42867-55-0; **7** 3,5-dinitrobenzoate, 42867-56-1; isopropyl alcohol, 67-63-0; 3,5-dinitrobenzoyl chloride, 99-33-2.

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Synthesis of Hydroxycitronellal. Hydration and Subsequent Hydrolysis of Imines, Enamines, or Oxazolidines Prepared from Citronellal and Amines

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Hydroxycitronellal (**4**), one of the most widely used synthetic perfumery materials, has been prepared from citronellal (**1**) by the hydration of citronellal bisulfite (**2**) in sulfuric acid and the subsequent hydrolysis with alkali (course A in Scheme I).[1] The process, however, is accompanied by the liberation of **1** from the adduct **2** and the cyclization of **1** to isopulegol (**5**), which is further hydrated to menthoglycol (**6**), as shown in Scheme I (course B).[2] Consequently, the yield of **4** is very poor.

The hydration of olefinic compounds to alcohols generally proceeds very fast in strong acidic media,[3] whereas the hydrolyses of some aldehyde–amine adducts, *i.e.*, imines,[4] oxazolidines,[5] and enamines,[6] have been reported to be relatively slow in strong acidic media and fast in weak alkaline solutions or in water. Imines and enamines have been used for protecting aldehyde grouping in the related citral system where sulfuric acid has been used for generating a carbonium ion to induce cyclization.[7] Thus, these amine adducts should be useful intermediates for protecting the aldehyde group of **1** in strong acid in order to prevent the side reaction shown in Scheme I (course B).

We have found a synthetic route to **4** which is superior in yield as well as in simplicity to the conventional method (Scheme II).[8]

Reactions of **1** with five primary amines gave the imines **7–10** and **18** (Table I). In the crude products prepared from **1** and ethanolamine, the presence of an oxazolidine derivative[9] as well as **8** was noticed from the newly observed νC–O–C band at 1020 cm^{-1} and the decreased absorption at 1060 cm^{-1} attributable to primary OH. The relatively great value (1669 cm^{-1}) of νC=N absorption in **9** suggests that the tautomerism described below does not take place.

$$C_6H_5CH_2N{=}CH{\sim} \rightleftharpoons C_6H_5CH{=}NCH_2{\sim}$$

The isolation of **10** and **18** by means of distillation resulted in the formation of undesirable resinous materials. Therefore, the crude adduct **18** was used for the synthesis of **4**.

Five enamines, **11–15**, were derived from aliphatic secondary amines (Table II). From two aliphatic secondary amines substituted with one or two 2-hydroxyethyl

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