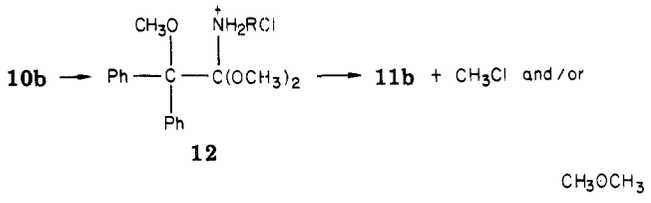
a 56% yield of gaseous products which is consistent with an ortho ester precursor such as **12** giving rise to the amide.[10]



In contrast to these results, Senō et al. have recently reported that the ring opening of some *gem*-dichloroaziridines with phenol, benzene, and a Lewis acid catalyst follows several different reaction pathways.[11]

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The nuclear magnetic resonance spectra were recorded on a Varian Associates T-60A spectrometer, using tetramethylsilane as an internal standard. Infrared spectra were determined in potassium bromide or as a neat liquid on a Perkin-Elmer 137 spectrophotometer. The microanalyses were preformed by Midwest Microlab, Ltd. Methanol was purified by distillation from magnesium methoxide, and ether was distilled from lithium aluminum hydride. These solvents were distilled under a dry nitrogen atmosphere and handled via a syringe by using the appropriate Schlenk techniques.

Methanolysis of *gem*-Dichloroaziridines. General Procedure. The *gem*-dichloroaziridine was placed into a two-necked flask fitted with a septum and condenser. The condenser was connected to a nitrogen-vacuum double manifold, and a dry nitrogen atmosphere was introduced. Dry methanol was added via a syringe, and the solution was heated at the reflux temperature. The methanol was removed via the vacuum manifold from the cooled reaction mixture. Dry ether was added via syringe, and the insoluble salt was isolated by filtration and washed with ether. The ether was removed in vacuo from the filtrate to afford the ether-soluble products.

Methyl ether and methyl chloride were isolated by using the same basic procedure with the exceptions that the methanol was introduced by vacuum transfer from a multipurpose vacuum line, and the reaction was run below ambient (ca. 600 mm) pressure. The gases were isolated on the vacuum line by using an ethyl acetate–liquid nitrogen slush (−83 °C), and the product ratio was determined by NMR.

Methanolysis of 1,3-Diphenyl-2,2-dichloroaziridine (1). A solution of 0.454 g (1.72 mmol) of **1** and dry methanol (7 mL) was heated at the reflux temperature for 40 min. Anilinium chloride (0.158 g, 71%) and 0.255 g (≃82%) of a mixture of esters **5** (29%) and **6** (71%) were isolated.[3] In a second reaction, a 49% yield of gas was isolated after several hours at the reflux temperature: methyl ether (26%) and methyl chloride (74%).

Methanolysis of 1-(1-Naphthyl)-3-phenyl-2,2-dichloroaziridine (9). By use of the above procedure, 320 mg (1.02 mmol) of the aziridine afforded 154 mg (91%) of 1-naphthylamine hydrochloride and 160 mg (≃90%) of the esters **5** (46%) and **6** (54%) (vide NMR). Methyl ether and methyl chloride were isolated in 49% yield in a 68:32 ratio, respectively.

Methanolysis of 1-Benzyl-3,3-diphenyl-2,2-dichloroaziridine (10b). By use of the above procedure, 270 mg (0.763 mmol) of **10b** and methanol were heated overnight. The ether-insoluble material (6 mg) was not identified, and 251 mg (99%) of crude **10b** (vide NMR) was obtained from the ether filtrate. Crystallization from hexane afforded 202 mg (80%) of the pure amide **11b** (mp 86–88 °C), and an analytical sample had the following: mp 87.5–88.5 °C; IR (KBr) 3375 (NH), 1650 cm^{-1} (C=O); NMR (CCl_4) δ 7.6–6.9 (m, 16, Ph and NH), 4.32 (d, 1, J = 6 Hz, CH_2N), 2.97 (s, 3, OCH_3).

Anal. Calcd for $C_{22}H_{21}NO_2$: C, 79.72; H, 6.40; N, 4.23. Found: C, 79.72; H, 6.27; N, 4.32.

In a second methanolysis reaction a 56% yield of gaseous products was isolated.

Pyrolysis of 1,3-Diphenyl-2,2-dichloroaziridine (1). The aziridine (ca. 0.5 g) was placed in a 25-mL round-bottomed flask fitted with a condenser. The condenser was connected to a nitrogen-vacuum double manifold, and a nitrogen atmosphere was introduced. Pyrolysis at 115–120 °C for ca. 1.5 h was sufficient for quantitative conversion to **7** (vide NMR). The addition of dry methanol (5 mL) afforded anilinium chloride (76%) and **5** (56%).

Methyl 2-Chloro-*N*,2-diphenylacetimidate (3). Pyrolysis of **1** with a methanol–methoxide quench afforded a 97% yield of crude **3** (vide NMR).

Methanolysis of 1,3,3-Triphenyl-2,2-dichloroaziridine (10a). Methanolysis of 0.536 g (1.58 mmol) of **10a** gave 378 mg (76%) of amide **11a** after a 2-h reaction period; mp 149–151 °C (lit.[12] mp 150.5–151.5 °C). Similar results were obtained by starting with the crystalline *N*,2,2-triphenyl-2-chloroacetimidoyl chloride.

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Registry No. **1**, 3543-98-4; **3**, 73178-69-5; **5**, 7476-66-6; **6**, 3558-61-0; **7**, 10295-39-3; **9**, 31528-95-7; **10a**, 972-14-5; **10b**, 31528-96-8; **11a**, 22050-98-2; **11b**, 73178-70-8; anilinium chloride, 142-04-1; methyl ether, 115-10-6; methyl chloride, 74-87-3; 1-naphthylamine hydrochloride, 552-46-5; *N*,2,2-triphenyl-2-chloroacetimidoyl chloride, 73178-71-9.

(10) Henri Ulrich, "The Chemistry of Imidoyl Halides", Plenum Press, New York, 1968, p 80.

(11) M. Senō, S. Shiraishi, H. Kise, and Y. Suzuki, *J. Org. Chem.*, **43**, 3402 (1979).

(12) H. H. Wasserman and P. S. Wharton, *J. Am. Chem. Soc.*, **82**, 3457 (1960).

Synthesis of 2-(Methoxycarbonyl)- and 2-(Acetoxymethyl)-3-isopropenyl-1-methylcyclopentene. Key Intermediates for the Synthesis of Iridoid Monoterpenes

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An attractive strategy for the synthesis of the iridoid monoterpenes, based on the cleavage and recyclization of limonene, was described by Wolinsky et al.[2] The products synthesized by this route, however, are the optical antipodes of the naturally occurring materials. Here we wish to describe a ready synthesis of the key intermediates **1** and **2** of Wolinsky's synthesis from racemic starting material (Scheme I).

Previously we reported[3] that anodic oxidative decarboxylation of the anion of **3**, readily obtained by the Diels–Alder reaction of 2,5-dimethylfuran and maleic anhydride followed by hydrogenation and methanolysis, led

(1) Department of Fine Arts, Kyoto City University of Arts, Kyoto 605, Japan.

(2) (a) J. Wolinsky and D. Nelson, *Tetrahedron*, **25**, 3767 (1969); (b) T. Sakan, S. Isoe, S. B. Hyeon, R. Katsumura, T. Maeda, J. Wolinsky, D. Dickerson, M. Slabaugh, and D. Nelson, *Tetrahedron Lett.*, 4097 (1965).

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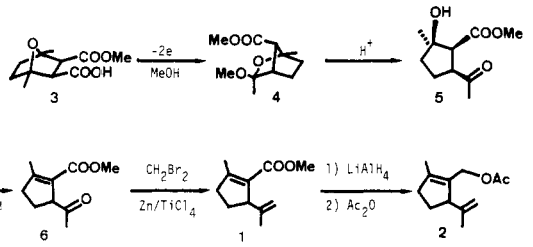
Scheme I



to the protected form 4 of methyl hydroxynepetonate (5) in good yield via Wagner–Meerwein rearrangement. This compound was chosen as a starting material for the present synthesis.

Methyl hydroxynepetonate (5), obtained by acidic hydrolysis of 4,[3] was dehydrated by phosphoryl chloride/pyridine to give a mixture of olefinic isomers. Treatment of the mixture with sodium methoxide in methanol gave a single isomer, 6. The reaction of 6 thus obtained with a reagent consisting of dibromomethane/zinc/titanium tetrachloride[4] afforded the diene 1 in excellent yield. It should be noted that the ester group does not interfere with this carbonyl methylenation reaction, which is not the case if the conventional Wittig methylenation procedure[5] is employed.

Lithium aluminum hydride reduction of 1 followed by acetylation gave 2 in high yield.

Since 1 and 2 can be readily transformed into a variety of iridoid monoterpenes such as matatabiether, neonepetalactone, and so on,[2] the synthesis by the above procedure constitutes a new and efficient route to these interesting substances.[6]

Experimental Section[7]

Methyl (±)-2-Methyl-5-acetylcyclopentene-1-carboxylate (6). To a stirred solution of 1.157 g (5.78 mmol) of methyl 2-hydroxy-2-methyl-5-acetylcyclopentane-1-carboxylate (methyl hydroxynepetonate) (5) in 20 mL of dry pyridine at 0 °C was added dropwise 4 mL (6.58 g, 42.9 mmol) of phosphoryl chloride. After being stirred at room temperature until the starting material disappeared, the reaction mixture was poured into ice water and extracted with dichloromethane. The organic layer was washed successively with dilute HCl, saturated aqueous $NaHCO_3$ solution, and brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield 0.984 g (93%) of an oil, GLC analysis of which showed two peaks.[8]

A solution of the above oily mixture (0.110 g, 0.60 mmol) in dry MeOH was stirred with a catalytic amount of sodium methoxide overnight at room temperature under a nitrogen atmosphere. After the solution was neutralized with aqueous AcOH, the solvent was removed in vacuo. The residue was dissolved in water, extracted with dichloromethane, and dried over anhydrous Na_2SO_4. Removal of the solvent gave 0.090 g (82%) of pure 6: IR (neat) 1710, 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (m, 1 H), 3.75 (s, 3 H), 2.40–2.70 (m, 2 H), 1.70–2.00 (m, 2 H), 2.25 (s, 6 H, $COCH_3$ and $=CHCH_3$); ^{13}C NMR ($CDCl_3$) δ 210.2 (s), 165.7 (s), 159.6 (s), 126.9 (s), 58.8 (d), 51.1 (q), 39.8 (t), 28.5 (q), 25.9 (t), 16.4 (q). Anal. Calcd for $C_{10}H_{14}O_3$: C, 73.30; H, 8.95. Found: C, 73.50; H, 9.17.

Methyl (±)-Isopropenyl-2-methyl-1-cyclopentene-1-carboxylate (1). To a suspension of Zn dust (0.392 g, 6.00 mmol) and dibromomethane (0.522 g, 3.00 mmol) in 10 mL of freshly distilled dry tetrahydrofuran was added a solution of $TiCl_4$ (2.20 mL of a 1.0 M dichloromethane solution, 2.20 mmol) at room temperature under nitrogen atmosphere. Instantaneous exothermic reaction occurred, and the color of the reaction mixture changed rapidly to dark brown. After the mixture was stirred for 15 min, a solution of 0.182 g (1.00 mmol) of 6 in 3 mL of tetrahydrofuran was added dropwise, and the mixture was stirrred overnight. The mixture was diluted with 10 mL of ether, washed with 20 mL of 1 N HCl and subsequently with 20 mL of brine and finally dried over anhydrous Na_2SO_4. Removal of the solvent gave 0.156 g (94%) of an oil. Spectroscopic data were identical with those reported:[2a] ^{13}C NMR ($CDCl_3$) δ 166.6 (s), 156.5 (s), 148.1 (s), 129.7 (s), 109.2 (t), 53.4 (q), 50.9 (d), 39.4 (t), 28.8 (t), 20.7 (q), 16.4 (q).

(±)-2-(Acetoxymethyl)-3-isopropenyl-1-methylcyclopentene (2). To a stirred suspension of 0.061 g (1.61 mmol) of $LiAlH_4$ in 10 mL of dry ether was added 0.114 g (0.63 mmol) of 1 in 10 mL of dry ether. After 3 h the reaction was quenched with saturated aqueous Na_2SO_4 solution. The mixture was filtered and the organic layer was dried over Na_2SO_4. Removal of the solvent gave an oily alcohol. The alcohol was dissolved in 20 mL of acetic anhydride and 4 drops of pyridine was added. The mixture was kept overnight at room temperature, then poured into water, and stirred. The mixture was extracted with ether and the organic layer was washed with water, saturated aqueous $NaHCO_3$ solution, and brine. Removal of the ether left 0.119 g (97%) of the acetate 2. Spectroscopic data were identical with those reported:[2b] ^{13}C NMR ($CDCl_3$) δ 171.0 (s), 147.6 (s), 141.2 (2 s), 110.8 (t), 59.5 (t), 48.0 (d), 37.8 (t), 27.9 (t), 20.8 (q), 18.9 (q), 14.1 (q).

Registry No. (±)-1, 73136-32-0; (±)-2, 73136-33-1; (±)-5, 73136-34-2; (±)-6, 73089-87-9; methyl 2-methyl-5-acetyl-2-cyclopentene-1-carboxylate, 73089-88-0; methyl 2-methylene-5-acetylcyclopentanecarboxylate, 73089-89-1.

(4) K. Takai, Y. Hotta, K. Oshima, and H. Nozaki, *Tetrahedron Lett.*, 2417 (1978).

(5) Attempted Wittig methylenation of 6 required preparative GLC separation and gave 1 only in 22% yield.

(6) Financial support of this work was provided by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan (No. 347074) (to M.K.) and by the Kawakami Foundation (to T.A.).

(7) IR spectra were determined with a Shimadzu IR-27 spectrometer. ^1H NMR spectra were measured with Varian EM-360 and EM-390 spectrometers and ^{13}C NMR spectra with a Varian CFT 20 spectrometer. Chemical shifts are given with reference to internal tetramethylsilane. GLC analyses were conducted with a PEG 20 M column (1 m) at 150 °C.

(8) Preparative LC separation [SiO_2; PhH/AcOEt (4:1) as eluant] gave pure 6 and another component in a ratio of 85:15. NMR spectral analyses of the latter enabled us to estimate that it was a mixture of methyl 2-methyl-5-acetyl-2-cyclopentene-1-carboxylate [^1H NMR δ 5.38 (1 H, m); ^{13}C NMR δ 125.6 (d)] and methyl 2-methylene-5-acetylcyclopentanecarboxylate [^1H NMR δ 5.02 and 5.10 (1 H each, both q of 2.3-Hz spacing); ^{13}C NMR δ 108.8 (t)] in a ratio of 4:3 (^1H NMR assay).

Cyclization–Rearrangement of Alkylstyrenes. 1. A. 1-Phenyl-1-pentene and Homologues. B. A Short Synthesis of Calamenene

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The preparation of 1,2,3,4-tetrahydronaphthalenes (tetralins) and indans by cyclodehydration of alcohols[1] or by acid-catalyzed ring closure of arylalkenes having a rationally placed double bond (e.g., 5-aryl-1- or -2-pentenes)[1c,2] is well-known. In pioneer work in this area, however, Bogert and co-workers obtained only polymer and

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