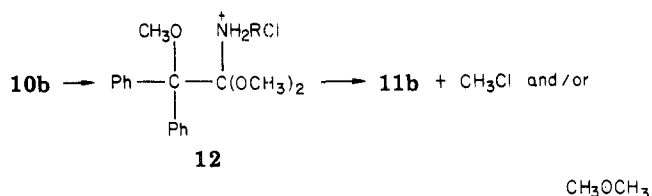


a 56% yield of gaseous products which is consistent with an ortho ester precursor such as 12 giving rise to the amide.¹⁰



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 performed 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 (CCl₄) δ 7.6–6.9 (m, 16, Ph and NH), 4.32 (d, 1, J = 6 Hz, CH₂N), 2.97 (s, 3, OCH₃).

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Anal. Calcd for C₂₂H₂₁NO₂: 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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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 reported³ 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

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