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Registry No. 3, 33614-96-9; 4, 73037-77-1; 5, 73037-76-0; 6, 73037-75-9; 7, 35797-77-4; 8a, 19052-86-9; 8b, 5726-14-7; 9a, 73037-79-3; 9b, 73037-78-2; 2-propanethiol, 75-33-2; thiophenol, 108-98-5; 1,2-ethanedithiol, 540-63-6; tropenylium tetrafluoroborate, 27081-10-3; Fe₂(CO)₉, 15321-51-4.

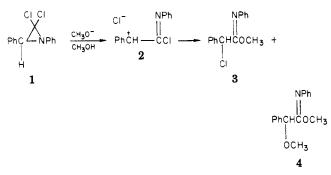
Haloaziridines. 3. Methanolysis of Some gem-Dichloroaziridines¹

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The methanolysis of 1,3-diphenyl-2,2-dichloroaziridine (1) has been reported to afford in high yield a mixture of the α -chloroimino ester 3 (38%) and the α -methoxyimino ester 4 (62%) in methanol-methoxide solution.³ These



products are consistent with those observed from hydrolysis,⁴ aminolysis,⁵ and pyrolysis⁶ of gem-dichloroaziridines, and carbonium ion 2 has been proposed as an intermediate in the formation of these products. In contrast to these results, the reaction of 1 in methanol in the absence of methoxide is reported to afford a mixture of esters 5 and 6 in the same approximate ratio as the ratio of 3 to 4 and anilinium chloride.³ Ichimura and Ohta have reported that the ethanolysis of 1 affords ethyl 2-chloro-2-phenylacetate and anilinium chloride.⁷

$$1 \xrightarrow{CH_3OH} PhCHClC(O)OCH_3 + 5$$

PhCH(OCH_3)C(O)OCH_3 + PhNH_3^+Cl⁻¹
6

The possible hydrolysis of the imino esters to 5 and 6 was tentatively eliminated by demonstrating their for-

(7) K. Ichimura and M. Ohta, Bull. Chem. Soc. Jpn., 40, 1933 (1967).

mation from 1 in high yield with anhydrous methanol. Since water was eliminated as the source of the carbonyl oxygen, the other logical source would be methanol, and an ortho ester intermediate has been proposed.⁷ Our initial attempts to observe an ortho ester intermediate by NMR spectroscopy of the reaction mixture were unsuccessful due to the five signals in the δ 3–5.5 region attributed to the products. The NMR spectrum of the reaction mixture was simplified by pyrolysis of 1 to the imidoyl chloride 7.

$$1 \rightarrow \text{PhCHClC}(\text{NPh})\text{Cl} \xrightarrow[\text{CH_0OH}]{} 5 + \text{PhNH}_3^+\text{Cl}^-$$

Quenching the imidoyl chloride 7 with anhydrous methanol afforded 5 and anilinium hydrochloride in high yield; however, absorptions attributable to an ortho ester intermediate were not observed.

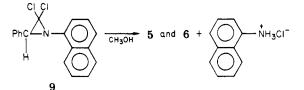
There is precedent for the formation of ortho esters from imidoyl chlorides⁸ and for the acid-catalyzed decomposition of ortho esters to esters.9 The decomposition of ortho ester intermediate 8 should form methyl ether and/or methyl ດບຸດບ

$$7 \xrightarrow{\text{CH}_3\text{OII}} \text{PhCHClC(OCH}_3)_3 + \text{HCl} \rightarrow \\ 8 \\ 5 + \text{CH}_3\text{OCH}_3 \text{ and/or CH}_3\text{Cl}$$

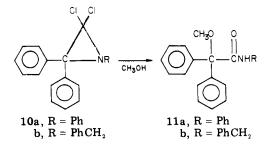
chloride. To determine if these gaseous products were formed, we examined the methanolysis of 1 on a multipurpose vacuum line, and a 50% yield of a mixture of methyl chloride and methyl ether was obtained in a 3:1 ratio, respectively.

The imino ester 3 was also prepared and converted to 5 under anhydrous reaction conditions and in the presence of small amounts of water. Consequently, the methanolysis of 1 appears to follow the typical ring-opening reaction to the expected imino esters. Reaction of the imino esters with methanol and the generated hydrogen chloride gives rise to 5 and 6.

The only reported alcoholysis reaction of a gem-dichloroaziridine in this series is 1. To determine the scope of this reaction, we examined the methanolysis of several additional gem-dichloroaziridines. The methanolysis of 1-(1-naphthyl)-3-phenyl-2,2-dichloroaziridine (9) gave the



expected mixture of 5 and 6 and naphthylamine hydrochloride in high yield. The methanolysis of 1,3,3-triphenyl-2,2-dichloroaziridine (10a) and 1-benzyl-3,3-diphenyl-2,2-dichloroaziridine (10b) afforded the amide 11 as the major product. The methanolysis of 10b afforded



(8) Robert H. DeWolfe, "Carboxylic Ortho Acid Derivatives", Academic Press, New York, 1970, Chapter 1. (9) See ref 8, p 146.

0022-3263/80/1945-2004\$01.00/0 © 1980 American Chemical Society

^{(1) (}a) Part 2: M. K. Meilahn, D. K. Olsen, W. J. Brittain and R. T. Anders, J. Org. Chem., 43, 1346 (1978); (b) presented at the American Chemical Society/Chemical Society of Japan Chemical Congress, April 2, 1979, Honolulu, HI, Abstract No. ORGN 47.

⁽²⁾ American Chemical Society-Petroleum Research Fund Scholar, 1978.

⁽³⁾ J. A. Deyrup and R. B. Greenwald, J. Am. Chem. Soc., 87, 4538 (1965).

^{(4) (}a) E. K. Fields and S. M. Sandri, Chem. Ind. (London), 1216 (1959); (b) R. E. Brooks, J. O. Edwards, G. Levey, and F. Smith, *Tetrahedron*, 22, 1279 (1966).
(5) M. K. Meilahn, L. L. Augenstein, and J. L. McManaman, J. Org.

Chem., 36, 3627 (1971).

^{(6) (}a) H. W. Heine and A. B. Smith, Angew. Chem., 2, 400 (1963); (b) see ref 1a

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

$$10b \longrightarrow Ph \longrightarrow C(0CH_3)_2 \longrightarrow 11b + CH_3Cl and/or$$

$$Ph \longrightarrow C(0CH_3)_2 \longrightarrow 11b + CH_3Cl and/or$$

$$Ph \longrightarrow 12$$

$$CH_3OCH_3$$

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 (\simeq 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 ($\simeq 90\%$) 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 etherinsoluble 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).

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.

(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 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

⁽¹⁰⁾ Henri Ulrich, "The Chemistry of Imidoyl Halides", Plenum Press, New York, 1968, p 80.
(11) M. Senö, S. Shiraishi, H. Kise, and Y. Suzuki, J. Org. Chem., 43,

^{3402 (1979).}

⁽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⁾ (3) T. Akiyama, T. Fujii, H. Ishiwari, T. Imagawa, and M. Kawanisi,

Tetrahedron Lett., 2165 (1978).