bubbled through the solution for 5 min. The solvent was removed under reduced pressure, and the oily green residue was extracted with two 50-ml portions of ethyl ether. The combined extracts were concentrated and chromatographed on alumina. Hexane eluted 1.0 g (67%) of yellow crystals of phenylacylferrocene (**7**), mp 81–82° (lit.[7] mp 80–82°). A small amount of highly polar material was not removed from the column. However, its R_f value was identical with that of glycol **6**.

B. **With Aluminum Oxide.**—Glycol **6** (1.6 g, 5 mmol) was intimately mixed with alumina (4.0 g) and placed in a vacuum sublimer equipped with a water-cooled probe. The system was evacuated and partially submerged in an oil bath for 8 hr at 150° (12 mm). Air was then admitted slowly and the yellow sublimate removed from the cold finger of the sublimer. The infrared and nmr spectra of this material were identical with those of phenacylferrocene (**7**) obtained in A. The total amount of **7** collected amounted to 1.0 g (67%), mp 80–81°. A tlc test of the alumina residue indicated a very small amount of **7** together with trace amounts of diketone **1**.

C. **With Aqueous Sulfuric Acid.**—The glycol **6** (1.61 g, 5 mmol) in 50 ml of acetone and 10 ml of 5% aqueous sulfuric acid solution was refluxed under nitrogen for 8 hr. The solution was cooled to room temperature, diluted with water, and extracted with ethyl ether. The ether portion was washed with water, 5% sodium bicarbonate solution, again with water, and was dried over anhydrous magnesium sulfate. Concentration of the solvent followed by chromatography on alumina using hexane as eluent produced 1.1 g (72%) of phenacylferrocene (**7**), mp 80–82°. No other ferrocene-containing products were detected.

Oxidation of Phenacylferrocene (7).—Phenacylferrocene (1.0 g, 3.3 mmol) and activated magnanese dioxide (5 g) were refluxed in methylcyclohexane (50 ml) for 2 hr. The mixture was cooled to room temperature and filtered. The residue was washed with two 10-ml portions of chloroform. The combined organic portions were concentrated and the residual red oil was crystallized from hexane as ruby red plates (1.0 g, 96%), mp 85–85.5°. A mixture melting point (on admixture with authentic **1**) was undepressed.

Addition of Phenyllithium to 1.—The diketone **1** (2.0 g, 6.3 mmol) was added in one portion to a stirred solution of phenyllithium (80 mmol) in 100 ml of ethyl ether under nitrogen. The mixture was allowed to stir for 3 hr, during which time the color changed from red to green and finally to gray. Water was added dropwise, and the mixture turned yellow. A tlc test (1:1 hexane–benzene) indicated a yellow band, which gradually transformed into a red band of lower R_f, and a colorless band of higher R_f. The ether portion was separated, dried over anhydrous magnesium sulfate, and evaporated to a red oil. Chromatography on alumina yielded the following products in the order cited. (1) Hexane eluted benzophenone, 1.0 g, mp 48–49°. A mixture melting point (on admixture with an authentic sample) was undepressed. (2) 1:1 Hexane–benzene eluted benzoylferrocene, 1.20 g, mp 108–109°. A mixture melting point (on admixture with an authentic sample) was undepressed.

When the gray solution was treated with methyl iodide, dry hydrogen chloride, or aqueous hydrochloric acid, benzophenone and benzoylferrocene were the only products isolated.

Registry No.—**1,** 12310-13-3; **4,** 12310-15-5; **5,** 12310-16-6; **6,** 12310-14-4.

Aziridines. XX. Isomerizations of 1-*p*-Nitrobenzoyl-2-vinylaziridine

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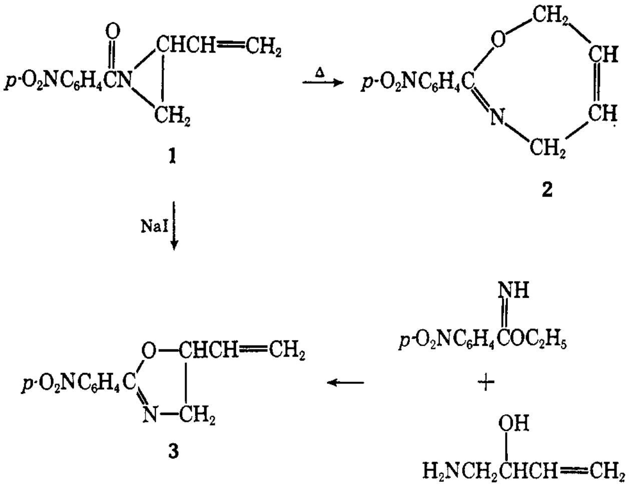
1-Aroylaziridines have been shown to undergo thermal rearrangements to 2-oxazolines, N-allylamides, and α-benzamidobenzalacetophenones. The course of the thermolysis depends in great part upon the substituents attached to the carbon of the aziridine ring. Thus 1-aroylaziridines unsubstituted on the aziridinyl carbons,[1-3] 1-aroyl-2,3-diarylaziridines,[4] and a few 1-aroylaziridines fused to another ring system[5,6] isomerize on heating to 2-oxazolines. 1-Acyl-2-alkylaziridines, on the other hand, almost always pyrolyze into N-allylamides[7] and 1,3-diaroyl-2-arylaziridines in refluxing *p*-xylene from α-benzamidobenzalacetophenones.[4]

We have now observed that 1-*p*-nitrobenzoyl-2-vinylaziridine (**1**) in refluxing toluene follows still another thermal pathway. The product of thermolysis is 2-*p*-nitrophenyl-4,7-dihydro-1,3-oxazepine (**2**). Tetrahydro- and hexahydro-1,3-oxazepines have been described, but **2** appears to be the first example of a dihydro-1,3-oxazepine. Compound **1** also reacted with iodide ion in acetone solution to give 2-*p*-nitrophenyl-5-vinyl-2-oxazoline (**3**). The iodide ion-catalyzed rearrangement of 1-aroylaziridines to 2-aryl-2-oxazolines is a well-known reaction.[4,8] The structure of **3** was confirmed by an alternate synthesis involving the reaction of 1-amino-3-buten-2-ol with ethyl *p*-nitrobenzimidate. Imido esters are known to react with amino alcohols to form 2-oxazolines.[9]

The nmr spectrum of **2** in $CDCl_3$ showed the *p*-nitrophenyl group as a quartet centered at 8.15 (4 H), the olefinic protons as a multiplet at 5.95 (2 H), and two other multiplets at 4.40 (2 H) and 4.80 ppm (2 H). The spectrum is similar to that of 4,6-dioxacycloheptene[10] which shows the olefinic protons as a multiplet at 5.74 ppm and the methylenes in the 3 and 7 positions as a multiplet at 4.32 ppm. On this basis the multiplet at 4.40 ppm in the spectrum of **2** can be assigned to the methylene next to the oxygen atom.



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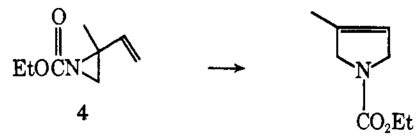
Recently it has been demonstrated that 1-carbethoxy-2-methyl-2-vinylaziridine (6) isomerizes when subjected to gas chromatography at 100° to 1-carbethoxy-3-methyl-3-pyrroline (5).[11]



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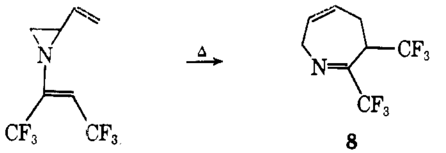
Although the nmr of 2 precluded the possibility of a symmetrical 3-pyrroline being formed during the thermolysis of 1, an authentic sample of 1-*p*-nitrobenzoyl-3-pyrroline (6) was prepared. Compound 6 was different from the product of rearrangement 2 in respect to nmr spectrum, infrared spectrum, and melting point. Compound 6 was also stable under the conditions of thermolysis of 1.

The thermal isomerization of 1 to 3 resembles the thermal rearrangement of 1-[1,2-bis(trifluoromethyl)]-vinyl-2-vinylaziridine (7) to 2,3-bistrifluoromethyl-3,4-dihydro-7H-azepine (8)[12] and the rearrangement of 1-*p*-bromophenyl-2-isopropenylaziridine (9) to 7-bromo-4-methyl-2,5-dihydro-1H-1-benzazepine (10).[13]



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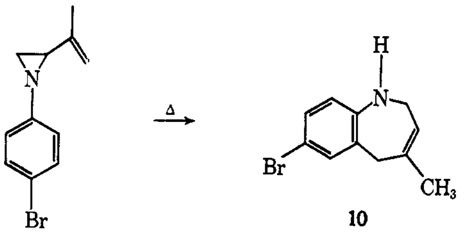

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Experimental Section

1-*p*-Nitrobenzoyl-2-vinylaziridine (1).—A solution of 1.86 g (0.01 mol) of *p*-nitrobenzoyl chloride in 20 ml of dry ether was added to a solution of 0.691 g (0.01 mol) of 2-vinylaziridine and 1.01 g (0.01 mol) of triethylamine in 150 ml of ether. The mixture was allowed to stand at room temperature for 2 hr and was filtered. The filtrate was evaporated to give 1.76 g of crude 1. Recrystallization three times from low-boiling petroleum ether gave 1 melting at 69–70°.

Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.61; N, 12.84. Found: C, 60.40; H, 4.45; N, 12.61.

The Thermal Isomerization of 1 into 2.—A solution of 125 mg of 1 in 10 ml of toluene was refluxed 4 hr. Evaporation of the solvent gave 121 mg of 2. Recrystallization of 2 from 95% ethanol formed crystals melting at 110–120°.

Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.61; N, 12.84. Found: C, 60.51; H, 4.72; N, 12.78.

The Iodide Ion Catalyzed Isomerization of 1 to 3.—A mixture of 312 mg of 1, 300 mg of sodium iodide, and 15 ml of acetone was kept at room temperature for 5 hr. The solvent was evaporated, and the residue was mixed with water. The crude 3 (305 mg) was filtered and recrystallized from 95% ethanol. Pure 3 melted at 94–96°.

Anal. Calcd for $C_{11}H_{10}N_2O_3$: C, 60.54; H, 4.61; N, 12.84. Found: C, 60.10; H, 4.57; N, 12.85.

Alternate Synthesis of 3.—A mixture of 0.108 g of ethyl *p*-nitrobenzimidate[14] and 0.044 g of 1-amino-3-buten-2-ol[15] was heated at 90–100° for 1.5 hr and then at 130–140° for 2 hr. The mixture solidified on cooling. Recrystallization from 95% ethanol gave 0.070 g of 3.

1-*p*-Nitrobenzyl-3-pyrroline (6) was prepared in an analogous manner as 1. After several recrystallizations from ethanol an analytical sample of 6 melted at 138–140°.

Anal. Calcd for $C_{11}H_{10}N_2O_3$: N, 12.84. Found: N, 12.82.

Registry No.—1, 17659-06-2; 2, 17659-07-3; 3, 17659-08-4; 6, 17659-09-5.

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Pseudohalogens. XIII.[1] Preparation and Properties of N-Monochlorourethan and Its Metallic Salts

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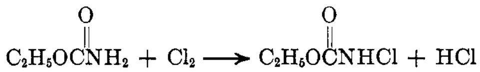
Attention is being given in our laboratory to the development of new and improved methods for the generation of nitrenes, and, in this connection, we have studied nitrene production from N-monochlorourethan (MCU) and its metallic salts by α-elimination reactions. MCU was first prepared by Datta and Gupta[3] and subsequently by Traube and Goekel,[4] and by Chabrier,[5] who also prepared some metallic salts, but explicit details concerning yields, methods of isolation, purity, and physical characteristics of the products were not reported.

In this Note we describe an improved method of preparation and the properties of MCU and several of its metallic salts, such as the sodium, potassium, and silver salts, and also attempts, unfortunately unsuccessful, to generate carbethoxynitrene by thermolysis of the salts in cyclohexene solution.

Preparation and Properties of MCU and Its Metallic Salts.—MCU can be readily prepared in about 50% yield by reaction of the calculated quantity of chlorine with an aqueous solution of ethylurethan at 5–10° (eq 1). Since MCU is insoluble in water, it precipitates



$$C_2H_5O\overset{O}{\overset{\|}{C}}NH_2 + Cl_2 \longrightarrow \underset{\text{MCU}}{C_2H_5O\overset{O}{\overset{\|}{C}}NHCl} + HCl \qquad (1)$$

as an oil, denser than water. Crude MCU is a pale yellow oil having a sharp odor; it contains a small amount of N,N-dichlorourethan (DCU). Assessment

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[2] To whom inquiries should be addressed. The authors acknowledge with thanks support of this investigation by U. S. Public Health Service Grants No. CA-07803, CA-07174, and CA-10439 of the National Cancer Institute.

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