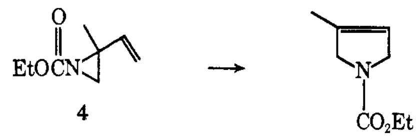
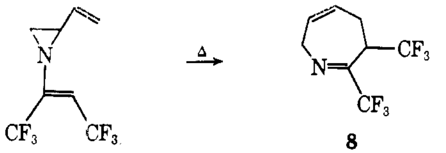
Recently it has been demonstrated that 1-carbethoxy-2-methyl-2-vinylaziridine (6) isomerizes when subjected to gas chromatography at 100° to 1-carbethoxy-3-methyl-3-pyrroline (5).[11]



4 5

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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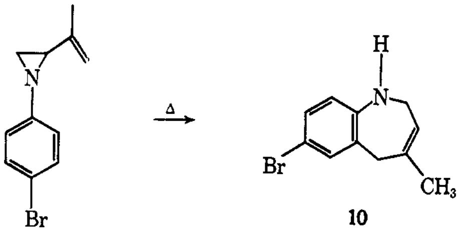

9 10

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, 4.57; 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.

Acknowledgment.—We thank Dr. E. L. Stogryn for a sample of 2-vinylaziridine and the National Institutes of Health for Grant CA-10015.

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[12] E. L. Stogryn and S. J. Brois, *J. Amer. Chem. Soc.*, **89**, 605 (1967).

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

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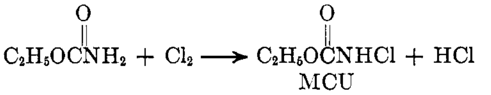
Received May 31, 1968

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



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

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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(1) Paper XII: T. A. Foglia and D. Swern, *J. Org. Chem.*, **33**, 4440 (1968).

(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.

(3) R. L. Datta and S. D. Gupta, *J. Amer. Chem. Soc.*, **36**, 386 (1914).

(4) W. Traube and H. Goekel, *Ber.*, **56B**, 384 (1923).

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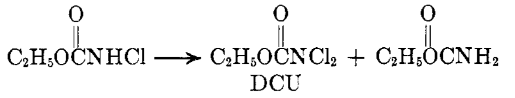
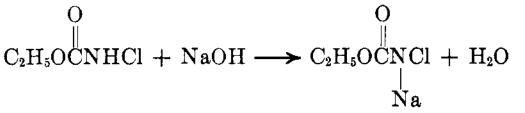
of the purity of MCU by iodometry gives a value slightly over 100% because of the DCU impurity. MCU of analytical purity, mp 9° and bp 44–45° (0.2 mm), is a colorless liquid obtained by distillation under high vacuum. High vacuum is very important in obtaining fair yields and high purity as it permits the distillation temperature to be as low as possible thus minimizing the disproportionation reaction shown in eq 2. Although separation of DCU from MCU is a facile process, ethylurethan sublimes with and contaminates the MCU.



$$C_2H_5O\overset{O}{\overset{\|}{C}}NHCl \longrightarrow \underset{DCU}{C_2H_5O\overset{O}{\overset{\|}{C}}NCl_2} + C_2H_5O\overset{O}{\overset{\|}{C}}NH_2 \qquad (2)$$

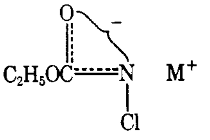
Iodometric analysis of crude and distilled MCU gives the total content of active chlorine. Composition of mixtures is readily determined by neutralization analysis as only MCU is a sufficiently strong acid to be titratable according to eq 3.



$$C_2H_5O\overset{O}{\overset{\|}{C}}NHCl + NaOH \longrightarrow C_2H_5O\overset{O}{\overset{\|}{C}}\underset{Na}{\underset{|}{N}}Cl + H_2O \qquad (3)$$

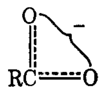
The analytically pure sodium or potassium salt of MCU can be obtained in quantitative yield by reaction of MCU with sodium or potassium hydroxide in methanol solution at 0°. Both salts are hygroscopic white crystalline solids which do not decompose on heating below 250°, contrary to literature reports.[5] When these salts are prepared from aqueous bases, anhydrous products are not obtained as water of crystallization is tightly bound. The analytically pure silver salt is obtained in quantitative yield by reaction of the sodium salt with silver nitrate in dilute aqueous solution at room temperature. When freshly prepared, it is a white crystalline solid which darkens on exposure to light and decomposes violently at or above about 127°. Attempts to isolate the lithium salt were unsuccessful.

The ir of neat MCU shows bands at 3300 (m) (N—H) and 1730 cm^{-1} (s) (C=O). In contrast, the ir of the metallic salts (KBr pellets) show no N—H absorption and the carbonyl shifts to 1600 cm^{-1} (s). The shift of the carbonyl absorption suggests that the metallic salts have the ionic structure



(M^+ = metal ion)

analogous to the carboxylate ion

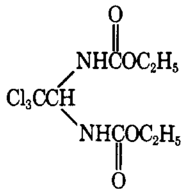


whose carbonyl band is at lower frequencies (about 150 cm^{-1}) than that of the esters.

The uv of MCU in methanol shows weak end absorption at 206 mμ (ε 118) and 245 (186) (C=O). The sodium salt shows a single peak of medium intensity at 205 mμ (ε 267) but the potassium salt absorbs much more strongly at 211 mμ (ε 1030).

Nmr spectral data of MCU and of its sodium and potassium salts are given in the Experimental Section. Since MCU reacts violently with DMSO-d_6 and the salts are insoluble in CCl_4, we could not directly compare the chemical shifts of MCU with those of its salts in the same solvent.

Reaction of Metallic Salts of MCU with Cyclohexene.—Thermolysis of the sodium and silver salts of MCU for 48 and 24 hr, respectively, in boiling cyclohexene gives only about 50% decomposition. Many side reactions occur, as shown by glpc. Some of the reaction products are ethylurethan, 1,1,1-trichloroethylbis(carbamate) (I) and azabicyclo[4.1.0]heptane (II), the last two in very low yield. These salts react with acetone to give diacetone alcohol and ethylurethan; the nature of the oxidation product(s) is unknown.



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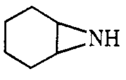

II

Experimental Section

Material and Equipment.—Ethylurethan was reagent grade obtained from Fisher Scientific Co. Chlorine gas, reagent grade, was obtained from a cylinder. Cyclohexene was distilled over metallic sodium before use. Ir spectra were obtained on a Perkin-Elmer Infracord, Model 137; uv spectra on a Perkin-Elmer ultraviolet–visible spectrometer Model 202. Nmr were obtained on a Varian A-60A spectrometer using TMS as internal standard. Refractive indices were taken on a Bausch and Lomb refractometer. Melting and boiling points are uncorrected. Microanalyses were performed by Micro-Analysis Inc., Wilmington, Del.

Iodometric Analysis.—Sufficient compound (0.1–0.2 g) was accurately weighed in an iodine flask to give a 10–15-ml titration with 0.1 *N* sodium thiosulfate. The sample was dissolved in 25 ml of water, and saturated sodium iodide solution (3 ml) was immediately added, followed by glacial acetic acid (5 ml). The solution was then titrated to a starch end point with 0.1 *N* sodium thiosulfate. A blank determination was run on the reagents.

Neutralization Analysis.—MCU (0.2–0.3 g) was accurately weighed and dissolved in 50 ml of methanol. An excess of 0.1 *N* NaOH was added, and the solution was back titrated with 0.1 *N* HCl using a pH meter. The neutralization points were determined from the usual graph.

Preparation of MCU.—An aqueous solution of ethylurethan (100 g, 1.125 mol) in water (500 ml) was placed in a 1-l. flask equipped with a stirrer, thermometer, and gas inlet tube. Chlorine gas (76 g, 1.07 mol), condensed from a cylinder, was allowed to distil slowly into the stirred solution over 4 hr at 5–10°. When chlorine addition was complete, the reaction mixture was allowed to separate into two phases and the lower organic phase was drawn off and washed successively with 20% aqueous sulfuric acid solution (two 100-ml portions) and water (two 100-ml portions). The crude MCU (69 g; 50 and 52% yield based on ethylurethan and chlorine, respectively), a pale yellow oil with a sharp odor, was then placed in a rotary vacuum evaporator to remove the last traces of water. The crude product contained a small quantity of DCU; iodometric analysis indicated a purity of 103% calculated as MCU. The oil was distilled through a Vigreux column (100 × 4 mm) under high vacuum. The main fraction (56 g) was collected at 44.0–45.0° (0.2 mm): mp 9°; $n^{25}D$ 1.4435. Iodometric and neutralization analyses indicated a purity greater than 99.4%: ir (neat) 3300 (NH), 1730 (C=O), 1440, 1380, 1330, 1240 (ester), 1070 (ester), and 765 (C—Cl) cm^{-1}; λ_{max} (CH_3OH) 206 mμ (ϵ 118) and 245 (186); nmr (CCl_4) δ 1.33 (t, 3, CH_3), 4.33 (q, 2, CH_2), and 6.95 ppm (broad s, 1, NH).

Sodium Salt of MCU.—To a methanol solution of sodium hydroxide (0.8 g, 0.02 mol), MCU (2.5 g, 0.02 mol) was added dropwise with stirring at 0°. When addition was complete, the reaction mixture was evaporated to dryness in a rotary vacuum evaporator at room temperature. The crude residue was washed with ether, and the residue was again evaporated to yield the anhydrous sodium salt, a hygroscopic white solid (2.7 g, 98.7% yield). Purity by iodometric analysis exceeded 99%. The salt did not decompose on heating to 250°: ir (KBr pellet) 1600 (C=O), 1360, 1260 (ester), 1080 (ester) and 770 (C—Cl) cm^{-1}; λ_{max} (CH_3OH) 205 mμ (ϵ 267); nmr (DMSO-d_6) δ 1.07 (t, 3, CH_3) and 3.83 ppm (q, 2 H, CH_2).

Potassium Salt of MCU.—Prepared from equimolar quantities of MCU and potassium hydroxide, as just described for the sodium salt, except that it was purified by pouring the half evaporated methanol solution into ether. The anhydrous potassium salt, a hygroscopic white solid, was obtained as a precipitate (yield 96%; purity >96%). It did not decompose on heating to 250°: ir (KBr pellets) 1600 (C=O), 1360, 1270 (ester), 1075 (ester) and 770 cm^{-1} (C—Cl); λ_{max} (CH_3OH) 211 mμ (ϵ 1030); nmr (DMSO-d_6) δ 1.05 (t, 3, CH_3) and 3.78 ppm (q, 2, CH_2).

Silver Salt of MCU.—A 1% aqueous solution of silver nitrate (1.2 g, 0.007 mol) was added dropwise to a 1% aqueous solution of the sodium salt of MCU (1.0 g, 0.007 mol) with stirring at room temperature in the dark. The precipitate was filtered, washed with methanol and dried under vacuum in the dark. A white crystalline solid unstable to light was obtained (yield 100%; purity >99.0%). The anhydrous silver salt decomposed violently on heating to 127°: ir (KBr pellets) 1600 (C=O), 1360, 1270 (ester), 1075 (ester) and 768 (C—Cl) cm^{-1}.

Lithium Salt of MCU.—Attempts to prepare the lithium salt were unsuccessful. Reaction of MCU at 0° with lithium hydroxide in methanol yielded an unstable colorless liquid that decomposed at room temperature with evolution of a gas over a period of several days. The freshly prepared oil gave a precipitate on treatment with aqueous silver nitrate suggesting that some lithium salt may have formed (MCU does not react with silver nitrate). Similar results were obtained on reaction of MCU with *n*-butyllithium at −76° in tetrahydrofuran with cyclohexene present.

Reaction of Metallic Salts of MCU with Cyclohexene.—A mixture of the sodium salt of MCU (10 g, 0.069 mol) and cyclohexene (282 g, 3.45 mol) was placed in a 500-ml flask equipped with a stirrer, thermometer, condenser, and gas inlet tube. The mixture was then refluxed under nitrogen for 48 hr. The insoluble matter was filtered, washed with ether, and dried under vacuum. It was shown by analysis to be a mixture of sodium chloride and the unreacted sodium salt of MCU. (By iodometric analysis, only 60% of the sodium salt of MCU had decomposed.) After removing ether and unreacted cyclohexene from the filtrate, the liquid residue was cooled to 0° to precipitate a very small yield of colorless needles. They were recrystallized from *n*-hexane and shown to be 1,1,1-trichloroethylbis(carbamate) (I): mp 172–172.5°; ir (KBr) 3260 (NH), 2990 (CH), 1700 (C=O) and 825 cm^{-1}; nmr ($CDCl_3$) δ 1.28 (t, 6, CH_3), 4.22 (q, 4, CH_2), 5.56 (broad, d, 2, NH), and 6.61 ppm (d, 1, CH).

Anal. Calcd for I: C, 31.24; H, 4.26; Cl, 34.58; N, 9.11; O, 20.81. Found: C, 31.42; H, 4.07; Cl, 34.85; N, 9.41; O, 20.15.

The hexane filtrate was washed with water to remove ethylurethan and then distilled under vacuum. A main fraction, azabicyclo[4.1.0]heptane, was obtained in very low yield at 31.0–32° (0.4 mm): ir (neat) 3350 (NH), 2920, 2850, 1440, 1020 and 882 cm^{-1}; nmr (CCl_4) δ 1.37 (m, ring CH_2), 1.79 (m, ring CH_2), 3.65 (broad s, ring CH), and 4.28 ppm (broad s, NH); singlet at 4.28 ppm disappears when the solution is treated with D_2O solution containing a trace of trifluoroacetic acid. The ir and nmr were identical with those of an authentic sample.

Reaction of the Sodium Salt of MCU with Acetone.—A mixture of the sodium salt (13 g, 0.089 mol) and acetone (254 g, 4.45 mol) was refluxed for 18 hr; 96% of the sodium salt decomposed. After sodium chloride was separated by filtration, the liquid product was distilled under reduced pressure; after removal of acetone a fraction was obtained as a colorless liquid (12 g) at 65.5–66.5° (13 mm), identified as diacetone alcohol by ir and nmr. The residue was dissolved in hot *n*-hexane and cooled to yield ethylurethan (4.9 g, 62% yield).

Registry No.—MCU, 16844-21-6; sodium salt of MCU, 17510-52-0; potassium salt of MCU, 17510-53-1; silver salt of MCU, 17510-54-2; I, 17528-34-6.

The Addition of Dimethylketene to Trichloroacetyl Chloride. A β-Keto Acid Halide[1]

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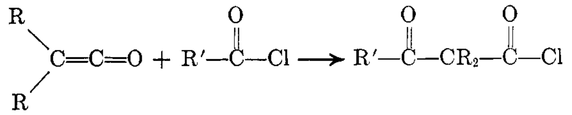
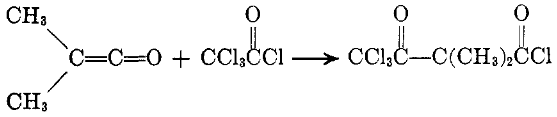
Received May 27, 1968

Staudinger and coworkers were the first to describe the addition of an acid chloride to a ketene to produce a β-keto acid halide[2] (eq 1). While this reaction has been investigated, in most cases the β-keto acid halide was not isolated but converted into an ester.[3,4] Therefore, we wish to report the results of an investigation on the addition of dimethylketene to trichloroacetyl chloride and the isolation, characterization, properties, and chemical reactivity of the resultant β-keto acid halide.



$$R_2C{=}C{=}O + R'{-}\overset{O}{\overset{\|}{C}}{-}Cl \longrightarrow R'{-}\overset{O}{\overset{\|}{C}}{-}CR_2{-}\overset{O}{\overset{\|}{C}}{-}Cl \quad (1)$$

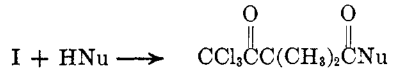
Dimethylketene readily reacts with trichloroacetyl chloride at room temperature to produce 4,4,4-trichloro-2,2-dimethyl-3-ketobutanoyl chloride (I) in 61% yield (eq 2). The structure of I was proven by a combination of elemental analysis and infrared (ir) and proton magnetic resonance (pmr) spectra. An ir band at 1785 revealed that the adduct was an acid halide and a band at 1740 cm^{-1} verified the presence of the β-keto group. The pmr spectrum revealed the methyl protons at 1.77 ppm.



$$(CH_3)_2C{=}C{=}O + CCl_3\overset{O}{\overset{\|}{C}}Cl \longrightarrow CCl_3\overset{O}{\overset{\|}{C}}{-}C(CH_3)_2\overset{O}{\overset{\|}{C}}Cl \quad (2)$$

I

Compound I readily undergoes the expected nucleophilic substitutions as illustrated in eq 3.



$$I + HNu \longrightarrow CCl_3\overset{O}{\overset{\|}{C}}C(CH_3)_2\overset{O}{\overset{\|}{C}}Nu \quad (3)$$

II, Nu = OCH_3
III, Nu = OH
IV, Nu = $NHCH_2C_6H_5$
V, Nu = NHC_6H_5

It is interesting to note that I reacts with an equimolar amount of benzylamine to produce the expected N-benzylamide (IV), but, when treated with an excess of amine, N,N′-dibenzyldimethylmalonamide (VI) is

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[1] This work was supported by a National Science Foundation Grant GP-7386.

[2] H. Staudinger, O. Gohring, and M. Scholler, *Ber.*, **47**, 40 (1914).

[3] F. Sorm, J. Smrt, and J. Beranek, *Chem. Listy.*, **48**, 679 (1954).

[4] F. Sorm, J. Smrt, and J. Beranek, *ibid.*, **49**, 73 (1955).