trans-**1-Isopropyl-2,3-dimethylaziridine.**—The compound was prepared from 12 g. (0.17 mole) of *trans*-2,3-epoxybutane: yield, 6 g., 31%; b.p. 102–102.5° (735 mm.); $n^{23.5}\text{D}$ 1.4019.

Anal. Calcd. for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37. Found: C, 74.23; H, 13.22; N, 12.12.

trans-**1-Isopropyl-2,3-dimethylaziridinium 2,4,6-Trinitrobenzenesulfonate.**—The salt was prepared as a derivative of the aziridine by adding a 10% solution of the aziridine in acetonitrile to a solution of 2,4,6-trinitrobenzenesulfonic acid in the same solvent until a distinct red coloration appeared. The red color was discharged by the addition of a small amount of the acid. After the product was precipitated by the addition of ether, it was recrystallized twice from absolute ethanol; m.p. 211.5–212.5°.

Anal. Calcd. for $C_{13}H_{18}N_4O_9S$: C, 38.42; H, 4.46; N, 13.79. Found: C, 38.41; H, 4.26; N, 14.09.

trans-**1,1,2,3-Tetramethylaziridinium Iodide.**—The salt was prepared by adding 2.1 g. (0.025 mole) of *trans*-1,2,3-trimethylaziridine to 25 ml. of methyl iodide which had been cooled to about −50°. White crystals began to form immediately. After about 10 min., when the mixture had reached room temperature, the crystalline solid was removed by filtration and air dried; yield, 5.4 g., 96%. The compound melted with decomposition in the region of 135–150°.

Since the methiodide could not be recrystallized without excessive decomposition, it was converted to the 2,4,6-trinitrobenzenesulfonate salt. To 0.050 g. (0.00125 mole) of silver trinitrobenzenesulfonate in 15 ml. of acetonitrile was added 0.301 g. (0.00125 mole) of the aziridinium iodide. Silver iodide (0.27 g.) precipitated immediately. The product was precipitated by the addition of about 500 ml. of anhydrous ether and recrystallized from acetonitrile–ether. The product melted at 205–206° dec.

Anal. Calcd. for $C_{12}H_{16}N_4O_9S$: C, 36.73; H, 4.11; N, 14.28. Found: C, 36.88; H, 4.44; N, 13.98.

trans-**1,1,2,3-Tetramethylaziridinium 2,4,6-Trinitrobenzenesulfonate.**—In an alternate procedure for the preparation of the trinitrobenzenesulfonate, 1.0 g. (0.0025 mole) of trimethyloxonium trinitrobenzenesulfonate[16] in 15 ml. of acetonitrile was added to 0.21 g. (0.0025 mole) of *trans*-1,2,3-trimethylaziridine in 15 ml. of acetonitrile. The solution was allowed to stand for 15 min. before precipitation of the product by the addition of about 500 ml. of anhydrous ether. The yields in this and subsequent analogous reactions were nearly quantitative. The infrared spectrum and melting point of the salt were identical with those of the product formed from the quaternary iodide. A mixture melting point showed no depression.

cis-**1-Ethyl-1,2,3-trimethylaziridinium Iodide.**—The compound was prepared by a method analogous to that described for the *trans*-tetramethylaziridine. Methyl iodide was used as the alkylating agent for the N-ethylaziridine. The iodide salt again was unstable and could not be recrystallized; m.p. 116–128° dec.

cis-**1-Ethyl-1,2,3-trimethylaziridinium Bromide.**—The bromide was prepared from the reaction between *cis*-1-ethyl-2,3-dimethylaziridine and methyl bromide in which the latter was the solvent. The highly hygroscopic product was purified by sublimation; m.p. 134–138° dec.

Anal. Calcd. for $C_7H_{16}BrN$: C, 43.31; H, 8.33; Br, 41.17. Found: C, 43.31; H, 8.68; Br, 40.73.

trans-**1-Ethyl-1,2,3-trimethylaziridinium Iodide.**—The compound was prepared directly from the aziridine and methyl iodide. The product decomposed on attempted recrystallization. Nitrogen analysis (calcd., 5.81%; found, 5.74%) was satisfactory, but the compound was converted to the trinitrobenzenesulfonate for further characterization.

trans-**1-Ethyl-1,2,3-trimethylaziridinium 2,4,6-Trinitrobenzenesulfonate.**—The compound was prepared by the alternative routes described for the corresponding N,N-dimethyl derivative. Both routes yielded identical products; m.p. 212–214° dec.

Anal. Calcd. for $C_{13}H_{18}N_4O_9S$: C, 38.42; H, 4.46; N, 13.79. Found: C, 38.71; H, 4.78; N, 14.08.

Equivalent Weight Determination.—Measurements were carried out with a Mechrolab Model 301A vapor pressure osmometer. The solutions were between 0.04 and 0.06 *F*, assuming the molecular weight of the monomer. Standard curves were determined with benzil and biphenyl as the solute in acetonitrile or ethanol.

D(+)-1,1,2,3-Tetramethylaziridinium Iodide.—The optically active iodide was prepared in the manner described for the inactive salt. It was used directly for kinetic measurements because of its instability on attempted recrystallization. The corresponding trinitrobenzenesulfonate could not be utilized because it also reacted with the ammonia or dimethylamine to be used for ring opening. The specific rotation of the iodide, $[\alpha]^{22}\text{D}$ +31.55°, was determined in ethanol. There was no change of rotation with time in solution, so no reaction with solvent was apparent. Even so, it was impossible to reisolate the compound in purer form.

meso-**Bis-2,3-dimethylaminobutane.**—The compound was isolated from the reaction mixture used for kinetic measurements. The reaction solution consisted of 0.050 g. of D(+)-1,1,2,3-tetramethylaziridinium iodide dissolved in 2.00 ml. of 3.32 *M* aqueous dimethylamine. After the solution had stood for 2 hr. at 25°, it was saturated with potassium hydroxide and extracted with ether. The ether solution was dried over potassium hydroxide pellets. The introduction of hydrogen chloride to the supernatant ether solution precipitated a white solid which was crystallized successively from ethanol and 1-propanol and sublimed. Because of inconsistent melting point characteristics and long melting point range, the hydrochloride was converted to the trinitrobenzenesulfonate by the addition of 2,4,6-trinitrobenzenesulfonic acid to an ethanolic solution and precipitation with ether. The product was recrystallized from acetonitrile containing a small amount of water; m.p. 263–264° dec.

Anal. Calcd. for $C_{20}H_{26}N_8O_{18}S_2$: C, 32.88; H, 3.59; N, 15.34. Found: C, 32.85; H, 3.62; N, 15.09.

(2*S*:3*R*)-2-Dimethylamino-3-aminobutane.—The compound was isolated as the hydrochloride from the solution used for kinetic measurements. The technique was that described for the bisdimethylamino product. The hydrochloride was very hygroscopic, but it was converted to a stable, easily handled compound by the addition of 2,4,6-trinitrobenzenesulfonic acid to an ethanolic solution. The trinitrobenzenesulfonate was crystallized from nitromethane–ether; m.p. 255–258° dec.

Anal. Calcd. for $C_{18}H_{22}N_8O_{18}S_2$: C, 30.77; H, 3.16; N, 15.95. Found: C, 30.50; H, 3.39; N, 15.70.

Kinetic Measurements.—The reactions of ammonia and dimethylamine with the optically active aziridinium iodide were followed polarimetrically at 400 mμ, using a J. C. Rudolph and Sons manual spectropolarimeter with an oscilloscope for readout. The temperature of all runs was kept at 25.0°. The reaction mixtures were prepared at the operating temperature and placed into a thermostated, 10-cm. polarimeter tube of all glass construction except for quartz windows. Measurements were made to ±0.003° rotation through at least three half-lives of the optically active reactant. The optical activity of the reactant and its concentration in solution were used to estimate the optical activity of products. In the case of the bisdimethylaminobutane, the lack of optical activity was verified by noting the lack of optical rotation of its dihydrochloride.

---

[16] D. J. Pettitt and G. K. Helmkamp, *J. Org. Chem.*, **28**, 2932 (1963).

Preparation of Oxamide from Hydrogen Cyanide and Hydrogen Peroxide

R. C. Sheridan and E. H. Brown

Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Alabama

Received September 1, 1964

Attfield[1] in 1863 and Radziszewski[2] in 1885 reported that hydrogen cyanide and hydrogen peroxide react to form oxamide, $(CONH_2)_2$, but Rupp and Pfennig[3] found that carbon dioxide and ammonia also are produced. The reaction to produce oxamide may be written

$$2HCN + H_2O_2 \longrightarrow (CONH_2)_2$$

---

[1] Attfield, *J. Chem. Soc.*, **16**, 94 (1863).

[2] B. Radziszewski, *Ber.*, **18**, 355 (1885).

[3] E. Rupp and F. Pfennig, *Chem. Ztg.*, **34**, 322 (1910).

but the reaction apparently proceeds in at least two stages such as

$$2HCN + H_2O_2 \longrightarrow (CN)_2 + 2H_2O$$
$$(CN)_2 + 2H_2O_2 \longrightarrow (CONH_2)_2 + O_2$$

or, over-all

$$2HCN + 3H_2O_2 \longrightarrow (CONH_2)_2 + 2H_2O + O_2$$

McMaster and Langreck[4] and Radziszewski[2] prepared several amides by the reaction

$$RCN + 2H_2O_2 \longrightarrow RCONH_2 + H_2O + O_2$$

and Wiberg[5] studied the preparation of benzamide from benzonitrile by this reaction. A brief study was made of the reaction of hydrogen cyanide with hydrogen peroxide in an exploration of methods for the preparation of oxamide.

Mixtures of aqueous solutions of hydrogen cyanide and hydrogen peroxide stand quietly with no apparent reaction for an induction period that decreases as the temperature of the cooling bath is raised. The mixtures then begin to effervesce, oxamide crystallizes, and the exothermic reaction becomes quite vigorous unless the mixture is cooled. The effect of the temperature of the cooling bath on the reaction is shown in Table I.

TABLE I

REACTION OF HYDROGEN CYANIDE WITH HYDROGEN PEROXIDE IN AQUEOUS SOLUTION[a]

Temp., °C		Time, min.		% of HCN converted to $(CONH_2)_2$
Bath	Max.	Induction	Reaction	
0	3	205	140	48.5
15	27	68	24	42.9
23	43	40	10	35.3
35	75	15	2	7.5

[a] Charge, moles: HCN 0.1253, H_2O_2 0.4944, H_2O 4.44.

In the runs reported in Table I, the mole ratio H_2O_2:HCN in the charge was 3.95. In tests at 0°, variation in this ratio from 1.65 to 4.70 made no significant difference in the fraction of hydrogen cyanide converted to oxamide (45 to 47%) or in the consumption of hydrogen peroxide, which ranged from 4.0 to 4.9 moles/mole of oxamide produced. Dilution of the reaction mixture with water increased the induction period and decreased the yield slightly.

The spent reaction mixtures contained hydrogen peroxide, but no hydrogen cyanide. The gases evolved during the reaction contained ammonia and carbon dioxide, indicating this side reaction.

$$HCN + H_2O_2 = CO_2 + NH_3$$

The oxamide was a homogeneous, white, crystalline product with the optical properties and powder X-ray pattern of the usual triclinic modification.[6]

Addition of the miscible organic solvents ethanol, methanol, dioxane, tetrahydrofuran, and acetone to the aqueous reaction mixture had no significant effect on the reaction, but N,N-dimethylacetamide both increased the induction period and decreased the yield of oxamide. Addition to the aqueous reaction mixture of small amounts of either sulfuric acid or potassium hydroxide decreased the yield of oxamide but had no effect on either the induction period or the rate of the reaction. Masson[7] reported that oxamide is not formed by the reaction of hydrogen peroxide with potassium cyanide.

When the reaction was carried out at 0° in nonaqueous solvents (ethyl acetate, amyl acetate, or isobutyl alcohol) the results were about the same as those obtained in aqueous solution: from 43.5 to 47.2% of the hydrogen cyanide was converted to oxamide, and 4.8 to 5.4 moles of hydrogen peroxide mole/of oxamide were consumed. The oxamide, however, appeared in a different crystal form which on recrystallization from water yielded the usual triclinic modification.[8]

Experimental

Stock solutions (usually about 10% HCN) were prepared from liquid hydrogen cyanide and chilled solvents. Aqueous hydrogen peroxide solutions were prepared by diluting reagent grade (30%) solutions; solutions of hydrogen peroxide in water-immiscible organic solvents were prepared by shaking mixtures of the solvents with 30% aqueous solutions of hydrogen peroxide and separating and discarding the aqueous phases. These solutions were then dried with anhydrous sodium sulfate and filtered.

Hydrogen cyanide in the stock solutions and spent reaction mixtures was determined by titration with silver nitrate, and hydrogen peroxide was determined by titration with potassium permanganate.

In each test of the reaction, the hydrogen cyanide and hydrogen peroxide solutions were mixed at the bath temperature in 250-ml. wide-necked volumetric flasks. The mixtures were allowed to stand in the cooling bath, with occasional swirling, until the reaction appeared to be complete; they were then filtered and the filtrates were analyzed for hydrogen cyanide and hydrogen peroxide. The precipitated oxamide was washed with small portions of ice-water, rinsed with acetone, dried at 105°, and examined by X-ray analysis.[6]

---

(4) L. McMaster and F. B. Langreck, *J. Am. Chem. Soc.*, **39**, 103 (1917).

(5) K. B. Wiberg, *ibid.*, **75**, 3961 (1953).

(6) E. M. Ayerst and J. R. C. Duke, *Acta Cryst.*, **7**, 588 (1954).

(7) O. Masson, *J. Chem. Soc.*, **91**, 1449 (1907).

(8) J. R. Lehr and E. H. Brown, *Nature*, **203**, 1168 (1964).

The Structure of the Dehydration Product, $C_{10}H_{14}O$, of 2-Hydroxyisopinocamphone[1]

Takayuki Suga, Kenichiro Mori, and Tamon Matsuura

Department of Chemistry, Faculty of Science,
Hiroshima University, Hiroshima, Japan

Received May 21, 1964

On dehydrating 2-hydroxyisopinocamphone[2] (1) with anhydrous oxalic acid, Kuwata[3] isolated a terpene ketone (b.p. 205–210°, n^{25}D 1.5034, $d^{25}{}_4$ 0.9450) along with the major product, carvacrol, and proposed it to be *p*-mentha-4(8),6-dien-2-one (**2**). The assignment of structure **2** was based on elementary analyses and nonidentity of the oxime, m.p. 103–104.5°, and semicarbazone, m.p. 183–184°, derivatives with derivatives in the literature. "Isocarvoxime" (**3**), m.p. 143–144°, the oxime derivative of **2**, has been synthesized from

---

(1) Supported in part by a grant from the Ministry of Education in Japan.

(2) The spatial arrangement of the hydroxyl group at C-2 has been clarified recently by H. Schmidt [*Chem. Ber.*, **93**, 2485 (1960)].

(3) T. Kuwata, *J. Soc. Chem. Ind. Japan*, **40**, 24 (1937); *Chem. Abstr.*, **31**, 3899^4 (1937).