was placed in a small vial and covered with 2 ml. of 3 *N* KOH. The vial was corked after being flushed with nitrogen gas. The vial and contents were placed in a water-bath at 50 ± 1° for forty-eight hours. After this period of time, the solution was made acid to phenol red and extracted with ether for thirty-six hours. About 5 ml. of water was added and the ether removed on a steam-bath. After the lactic acid was steam distilled to remove volatile impurities, it was degraded by the method of Wood, Lifson and Lorber.[8] Starting with 100 mg. of glucose, about 45 mg. of lactic acid was obtained. The lactic acid was determined by the method of Friedemann.[9] The C^{14} values are expressed in millimicrocuries (1×10^{-3} microcuries) per milligram of carbon.

TABLE I

DEGRADATION OF C^{14} LACTIC ACID FORMED DURING THE ACTION OF 3 *N* KOH ON GLUCOSE

Carbohydrate	Carbon Atoms of Lactic Acid COOH	CHOH	CH_3
3,4-C^{14}-D-glucose	8.73	0.69	3.64
1-C^{14}-D-glucose	3.60	0.22	3.60

(8) Wood, Lifson and Lorber, *J. Biol. Chem.*, **159**, 475 (1945).
(9) Friedemann, *ibid.*, **76**, 75 (1928).

Acknowledgment.—The author wishes to acknowledge the capable assistance of Mrs. Frances A. Bennett in these experiments.

Summary

1. The action of 3 *N* KOH on 1-C^{14}-D-glucose gave an equal distribution of label in the carboxyl carbon and beta carbon of lactic acid. This is in agreement with the theory of Evans.

2. During the action of 3 *N* KOH on glucose, about 42% of the lactic acid was derived from carbon atoms 1, 2 and 3 of glucose while the lower half of glucose yielded 58% of the lactic acid.

3. The action of 3 *N* KOH on 3,4-C^{14}-glucose yielded more activity (2.4:1) in the carboxyl carbon than in the beta carbon of lactic acid. This is not in agreement with the theory of Evans. The significance of this ratio was discussed.

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The Hydrolysis of 1-Nitro-4-methyl-2-nitramino-2-imidazoline

BY A. F. MCKAY[1] AND S. J. VIRON

Previously, it was reported[2] that although 1-nitro-2-nitramino-2-imidazoline had good power as an explosive, its sensitivity and ease of hydrolysis were detrimental to its use. It was found later that 1-nitro-2-nitramino-4-methyl-2-imidazoline[3] (I) also hydrolyzes readily. Since a knowledge of the course of hydrolysis of the latter compound might prove of importance as an aid in the syntheses of compounds of this series with greater stability, its behavior on hydrolysis was investigated.

When 1-nitro-2-nitramino-4-methyl-2-imidazoline (I) is refluxed with water three different compounds are obtained. One of the products, 1-nitro-4-methyl-2-imidazolidone (II) was identified by nitration to the known compound 1,3-dinitro-4-methyl-2-imidazolidone[4] (V). The second compound 1-(1-methyl-2-nitraminoethyl)-3-nitrourea (III) was converted to 1-(1-methyl-2-nitraminoethyl)-3-phenylurea by the method of T. L. Davis and K. Blanchard.[5] This same compound was obtained by treating 1-nitro-4-methyl-2-imidazolidone with aniline. If 1-nitro-2-nitramino-4-methyl-2-imidazoline (I) is completely hydrolyzed or 1-nitro-4-methyl-2-imidazolidone (II) and 1-(1-methyl-2-nitraminoethyl)-3-nitrourea are hydrolyzed, the end-product is 2-amino-3-nitraminopropane (IV).

(1) Defence Research Chemical Laboratories, Ottawa, Ontario.
(2) A. F. McKay and G. F Wright, THIS JOURNAL, **70**, 3990 (1948).
(3) A. F. McKay, R. H. Hall and G. F Wright, *ibid.*, in press.
(4) A. F. McKay and D. F. Manchester, *ibid.*, **71**, 1970 (1949).
(5) T. L. Davis and K. Blanchard, *ibid.*, **51**, 1790 (1929).

Attempts to convert 1-(1-methyl-2-nitraminoethyl)-3-nitrourea (III) into 1-nitro-4-methyl-2-imidazolidone (II) in aqueous solution were unsuccessful. Thus the hydrolysis of 1-nitro-2-nitramino-4-methyl-2-imidazoline follows two routes to the product 2-amino-3-nitraminopropane (IV) one through compound (II) and the other through compound (III).

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Experimental[6]

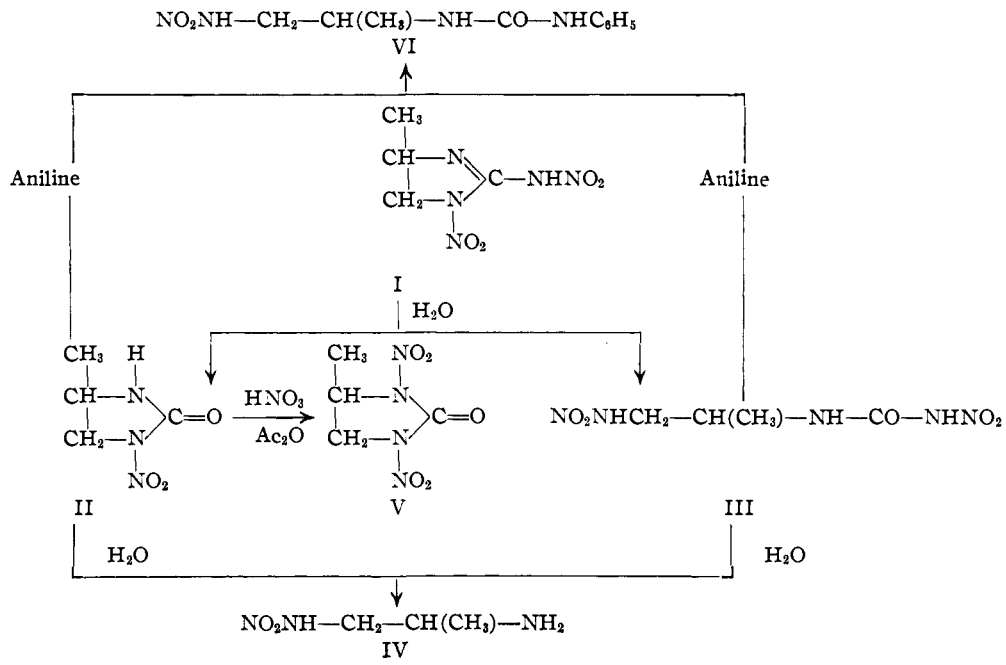
1-Nitro-2-nitramino-4-methyl-2-imidazoline.—1-Nitro-2-nitramino-4-methyl-2-imidazoline (m. p. 121.5–123.6°) was prepared in 63.3% yield by a previously described method.[4]

Hydrolysis of 1-Nitro-2-nitramino-4-methyl-2-imidazoline.—The hydrolysis of 1-nitro-2-nitramino-4-methyl-2-imidazoline (25 g., 0.132 mole) was accomplished by refluxing with 125 cc. of water, until all the solid had dissolved. After refluxing for a further period of fifteen minutes, the solution was cooled to room temperature and concentrated *in vacuo* to *ca.* 5 cc. A white solid (12.7 g.) separated which melted at 94.6–119.2° with decomposition. Three crystallizations from nitromethane (1 cc./g.) raised the melting point to 124.5–125° with decomposition. This product was identified as 1-(1-methyl-2-nitraminoethyl)-3-nitrourea.

Anal. Calcd. for $C_4H_9N_5O_5$: C, 23.2; H, 4.34; N, 33.8. Found: C, 23.2; H, 4.52; N, 33.3.

The filtrate from the first nitromethane crystallization was evaporated almost to dryness after which a second crop of crystals (m. p. 124.6–128.9°) was obtained, yield 2.3 g. (12.0%). This material was crystallized from ethyl

(6) All melting points are uncorrected.



acetate (1.5 cc./g.) to give 1-nitro-4-methyl-2-imidazolidone melting at 133–134°.

Anal. Calcd. for $C_4H_7N_3O_3$: C, 33.1; H, 4.82; N, 28.9. Found: C, 33.3; H, 4.83; N, 28.7.

A second experiment in which 10 g. (0.052 mole) of 1-nitro-2-nitramino-4-methyl-2-imidazoline was refluxed with 50 cc. of water was completed. The refluxing was continued for two hours after the crystals had dissolved. The clear solution was evaporated *in vacuo* to *ca.* 5 cc. and cooled to room temperature. The white solid was removed by filtration and extracted with hot acetone (25 cc.). An acetone insoluble fraction (0.63 g., 10.1% yield) was obtained which melted at 227–235° with decomposition. This product was purified by dissolving in water (10 cc./g.), adding ethanol (15 cc./g.) and cooling to −26°. Two crystallizations in this manner raised the melting point of the 2-amino-3-nitraminopropane to 239.5–240.9° with decomposition.

Anal. Calcd. for $C_3H_9N_3O_2$: C, 30.2; H, 7.56; N, 35.3. Found: C, 30.4; H, 7.63; N, 35.7.

The acetone filtrate was evaporated to dryness and the residue dissolved in hot nitromethane (2 cc.). On cooling to room temperature, 0.91 g. (11.8%) of crystalline material (m. p. 127.6–132.4°) was obtained. The melting point was raised to 133.8–134.7° by two crystallizations from ethyl acetate (1.5 cc./g.). A mixed melting point determination with a sample of 1-nitro-4-methyl-2-imidazolidone was not depressed.

1,3-Dinitro-4-methyl-2-imidazolidone.—1,3-Dinitro-4-methyl-2-imidazolidone (m. p. 99.9–100.8°) was prepared from 1-nitro-4-methyl-2-imidazolidone in 15.3% yield by a previously described method.[3] The product was identified by a mixed melting point determination with an authentic sample.

2-Amino-3-nitraminopropane.—When 1-nitro-4-methyl-2-imidazolidone and 1-(1-methyl-2-nitraminoethyl)-3-nitrourea were refluxed with water until gassing ceased, 2-amino-3-nitraminopropane was recovered from the clear solution on evaporation. One of the gases evolved in this reaction was identified as carbon dioxide.

1-(1-Methyl-2-nitraminoethyl)-3-phenylurea: from 1-Nitro-4-methyl-2-imidazolidone.—1-Nitro-4-methyl-2-imidazolidone (0.2 g., 0.0014 mole) was dissolved in 10 cc. of water and three mole equivalents of aniline were added. This reaction mixture was refluxed for forty-five minutes and then cooled to room temperature. The crystals (m. p. 190–192.3° with decomposition) were filtered off and washed with water, yield 0.26 g. (79.5%). Two crystallizations from ethanol (10 cc./g.) raised the melting point to 192.6–193.2°.

Anal. Calcd. for $C_{10}H_{14}N_4O_3$: C, 50.4; H, 5.49; N, 23.5. Found: C, 65.0; H, 5.69; N, 23.3.

From 1-(1-Methyl-2-nitraminoethyl)-3-nitrourea.—1-(1-methyl-2-nitraminoethyl)-3-phenylurea was obtained in 80.6% yield from 1-(1-methyl-2-nitraminoethyl)-3-nitrourea using the method described above.

Summary

The hydrolytic products of 1-nitro-4-methyl-2-nitramino-2-imidazoline have been isolated and identified.

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