phthalate, water, ligroin, *s*-butyl chloride) were all found to be selectively adsorbed on nitrocellulose. An expression is given for the activity of nitrocellulose as a function of its concentration and of the solvent additive.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

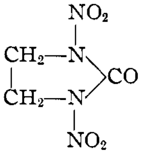
The Nitration of Derivatives of Ethylenediamine[1]

BY W. E. BACHMANN, W. J. HORTON,[2a] E. L. JENNER,[2b] N. W. MACNAUGHTON[2c] AND C. E. MAXWELL, III[2d]

Various methods were investigated for preparing the high explosive ethylenedinitramine (hereinafter called EDNA), $NO_2NHCH_2CH_2NHNO_2$, from ethylenediamine. EDNA has been prepared previously by hydrolysis of 1,3-dinitro-2-imidazolidone (I), which can be made by nitration of 2-imidazolidone. Fischer and Koch[3] prepared 2-imidazolidone by heating a mixture of anhydrous ethylenediamine and diethyl carbonate in a sealed tube; the yield was low and the product was difficult to purify. Moreover, the preparation of anhydrous ethylenediamine is a tedious process. We found that 2-imidazolidone could be obtained in 63% yield (based on the diethyl carbonate) from commercial aqueous 60–65% ethylenediamine without the use of a sealed-tube reaction. A mixture of excess aqueous ethylenediamine and diethyl carbonate was heated, the excess of reagents and water was removed by distillation, and the residue, presumably the ethylenemonourethan, $H_2NCH_2CH_2NHCOOC_2H_5$, was cyclized by the action of heat.[4]

By the method of Franchimont and Klobbie[5] and of Backer[6] with modifications, EDNA was prepared from aqueous ethylenediamine in an over-all yield of 87%. In this method ethylenebisurethan, prepared from aqueous ethylenediamine and ethyl chlorocarbonate, was nitrated with 98% nitric acid, and the dinitroethylenebisurethan (II) was converted into EDNA by alkaline hydrolysis or by ammonolysis. The rapid rate of the reaction of II with aqueous ammonia at room temperature is noteworthy; in a few minutes the carbethoxy groups are removed and the water-soluble ammonium salt of EDNA is formed.

EDNA was obtained also in good yield from the diacetyl derivative of ethylenediamine, which was prepared readily from aqueous ethylenediamine and acetic anhydride. Unlike the previous two derivatives of ethylenediamine, ethylenebisacetamide did not yield the dinitro derivative when treated with 98% nitric acid alone or mixed with concentrated sulfuric acid. A mixture of 98% nitric acid and acetic anhydride nitrated the compound smoothly. The dinitro derivative (III) was converted rapidly into EDNA by aqueous ammonia.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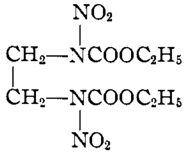
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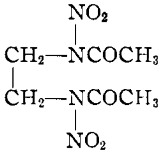
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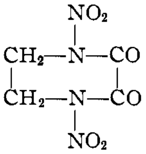
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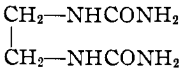
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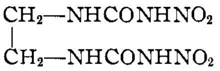
VI

The powerful aid to nitration offered by acetic anhydride was again manifested in the nitration of cyclic ethyleneoxamide. van Alphen,[7] who was the first to succeed in preparing cyclic ethyleneoxamide from ethylenediamine and diethyl oxalate, found that the compound was unaffected by absolute nitric acid at 0°; by nitration at 100° he obtained a microcrystalline powder in unspecified yield which melted indefinitely at about 150° with decomposition. We obtained the dinitro derivative (IV) in good yield in the form of glistening prisms with m. p. 197–198° by nitration of cyclic ethyleneoxamide (contaminated with linear polymers) by means of 98% nitric acid and acetic anhydride at 0–5°. Ammonolysis of the dinitro compound proceeded rapidly with the formation of EDNA and oxamide.

The possibility of utilizing ethylenebisurea (V) for preparing EDNA was investigated. The only practical methods which had been described for preparing V were the reaction of ethylenediamine dihydrochloride and potassium cyanate[8] and the interaction of ethylenediamine and nitrourea.[9] We found that ethylenebisurea was

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[1] This investigation was carried out under a contract recommended by the NDRC between the OSRD and the Regents of the University of Michigan, 1940.

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[3] Fischer and Koch, *Ann.*, **232**, 227 (1885).

[4] For later preparations of 2-imidazolidone see Mulvaney and Evans, *Ind. Eng. Chem.*, **40**, 393 (1948).

[5] Franchimont and Klobbie, *Rec. trav. chim.*, **7**, 258 (1888).

[6] Backer, *ibid.*, **31**, 171 (1912).

[7] van Alphen, *Rec. trav. chim.*, **54**, 937 (1935).

[8] Dox, THIS JOURNAL, **55**, 1230 (1933).

[9] Davis and Blanchard, *ibid.*, **51**, 1790 (1929).

formed in over 90% yield when an aqueous solution of ethylenediamine and urea was refluxed. Nitration of ethylenebisurea with 98% nitric acid and by the action of concentrated sulfuric acid and of acetic anhydride on the dinitrate salt gave a dinitro derivative (VI) with the nitro groups attached to the terminal nitrogen atoms. The structure of the product was proved by the following properties: solubility in aqueous alkali (presence of $NHNO_2$ group), reaction with aqueous ammonia to give ethylenebisurea (and not EDNA), and reaction with hot aniline to form 3,3'-diphenyl-1,1'-ethylenebisurea, $C_6H_5NHCONHCH_2CH_2NHCONHC_6H_5$. The nitration of ethylenebisurea is similar to that of N-ethylurea, which is nitrated at the NH_2 group, and differs from that of N-methylurea, which is nitrated on the nitrogen atom holding the alkyl group.

Experimental

2-Imidazolidone.—A mixture of 500 g. (5 moles) of 60% aqueous ethylenediamine and 118 g. of diethyl carbonate was refluxed for five hours and then heated on a steam-bath under reduced pressure (15–25 mm.) with a downward condenser until distillation ceased. The flask was then heated in an oil-bath (bath temperature, 180°) at atmospheric pressure; over a period of two hours the temperature of the vapor rose to 102° and then dropped. By extraction of the residue, which solidified on cooling, with 350 cc. of hot acetone, 54.8 g. of 2-imidazolidone suitable for nitration was isolated. A sample of recrystallized product melted at 132–132.5° (reported,[3] 131°).

A mixture of 17.1 g. of 1,3-dinitro-2-imidazolidone (m. p. 211–212°), prepared by nitration[10] of 2-imidazolidone, and 150 cc. of water was heated on a steam-bath with occasional swirling for one and one-half hours. The chilled, filtered solution deposited 13.1 g. (90%) of EDNA; m. p. 174.5–176° (reported 174.5–175°).

Preparation of EDNA from Ethylenebisurethan.—A 1-l. flask containing 23.2 g. of 65% aqueous ethylenediamine and 75 cc. of water and fitted with a thermometer, a Hershberg stirrer, and two burets was immersed in an ice–salt bath. One buret contained 48 cc. of ethyl chlorocarbonate, the other 96 cc. of an aqueous solution containing 21 g. of sodium hydroxide. Two cc. of ethyl chlorocarbonate was added slowly to the stirred solution in the flask, and then the remainder was added simultaneously with the sodium hydroxide solution (2 cc. of the latter to 1 cc. of ethyl chlorocarbonate) at such a rate that the temperature did not rise above 5° (about seventy-five minutes were required). After the mixture had been stirred for another hour at 5°, the ethylenebisurethan was collected on a filter and washed with 50 cc. of cold water (the product is soluble in water to the extent of 2%); yield, 50.3 g.; m. p. 108.5–110.5° (reported, 112°,[3] 113°[11]) to a liquid which was cloudy because of the presence of a few per cent. of salt. The product was suitable for nitration; it could be separated from salt by hot benzene; corrected yield, 48.9 g. (96%).

About fifteen minutes were required for the addition of 21.4 g. of ethylenebisurethan to 71 cc. of stirred colorless 98% nitric acid below 5°. The mixture was stirred well with 75 g. of ice and 100 cc. of water, and the dinitroethylenebisurethan (II) was collected and washed well with water; yield, 29.5 g. (95%); m. p. 82–82.5° (reported,[5] 83–84°).

When a mixture of 29.6 g. of the dinitro derivative, 28 cc. of water and 28 cc. of 28% aqueous ammonia was swirled, a practically clear, warm solution resulted in a few minutes. After being heated on a steam-bath for a few minutes the solution was filtered and treated with 25 cc. of concentrated hydrochloric acid; yield of EDNA, 14.1 g.; m. p. 174.5–176°.

A similar result was obtained by hydrolysis with a solution of 9.6 g. of sodium hydroxide in 34 cc. of water. The stirred mixture was heated on a steam-bath; a vigorous reaction set in as soon as the dinitro derivative became emulsified and was complete in ten minutes. Backer[6] obtained a high yield of the dinitro derivative of the methyl ester, which he treated with ammonia in ethanolic solution.

Nitration of Ethylenebisacetamide.—Acetic anhydride (750 cc.) was added from a dropping funnel to 280 g. of 64% aqueous ethylenediamine with stirring and cooling. The clear solution was concentrated on a steam-bath in a current of air, an equal volume of acetone was added, and the hot mixture was cooled. A first crop (403 g., m. p. 172–173°; reported[12] 175°) and a second crop (112 g., only slightly less pure) of ethylenebisacetamide were collected.

Acetic anhydride (40 cc.) was added slowly with stirring to 40 cc. of 98% nitric acid cooled in an ice–salt-bath at such a rate that the temperature did not rise above 5°. The mixture (which should be used immediately) was kept below 5° during the portion-wise addition of 15 g. of ethylenebisacetamide; toward the end of the addition the product began to precipitate from the solution. After six hours at 5°, the mixture was treated with about 250 g. of ice and the **N,N'-dinitroethylenebisacetamide** (III) was collected; yield, 20.1 g. (83%); m. p. 132–133°. The compound crystallized from acetone in thin colorless plates; m. p. 135.5–136° dec.

Anal. Calcd. for $C_6H_{10}N_4O_6$: C, 30.8; H, 4.3. Found: C, 30.3; H, 4.2.

A clear solution was formed in a short time when a mixture of 46.8 g. of the dinitro derivative and a solution of 34 g. of sodium hydroxide in 100 cc. of water was stirred vigorously. Addition of 100 cc. of concentrated hydrochloric acid followed by cooling precipitated 28.2 g. (94%) of EDNA; m. p. 179–180° cor. Similarly a 91% yield of EDNA was obtained by stirring 10 g. of the dinitro compound with 27 cc. of concentrated aqueous ammonia and an equal volume of water. Hydrolysis by boiling water was unsatisfactory.

Nitration of N,N'-Ethyleneoxamide.—The addition of 15 g. of N,N'-ethyleneoxamide[7] (which melted only partially at 275–285° on account of the presence of linear polymer) to a mixture of 40 cc. each of 98% nitric acid and acetic anhydride was carried out as described for III. After twenty hours in a refrigerator, the **N,N'-dinitroethyleneoxamide** (IV) was collected on a filter and washed with acetic acid; yield, 16.6 g.; m. p. 180–185°. The compound crystallized from ethyl acetate and from a small volume of acetone in colorless prisms; m. p. 197–198° dec. when placed in the bath at 190°.

Anal. Calcd. for $C_4H_4N_4O_6$: C, 23.5; H, 2.0. Found: C, 23.9; H, 2.2.

A mixture of 8 g. of the dinitro compound, 10 cc. of water and 10 cc. of 28% aqueous ammonia was warmed on a steam-bath for a few minutes, and the solution was filtered from oxamide (2 g.) and acidified; yield of EDNA, 5.2 g.; 175.5–177° cor.

Preparation and Nitration of Ethylenebisurea.—A solution of 1000 g. of urea in 875 g. of 60% aqueous ethylenediamine was refluxed for three hours; during this time ammonia was evolved. The hot solution was poured into a liter of 95% ethanol; the chilled solution deposited 1188 g. (97%) of 1,1'-ethylenebisurea; m. p. 188°. After digestion with 2 liters of hot ethanol and cooling, 1085 g. (89%) with m. p. 190–191° remained. After recrystallization from aqueous alcohol a sample melted at 192–193° (reported,[9] 193–194°).

The clear solution of 1.46 g. of ethylenebisurea in 3.6 cc. of 98% nitric acid at 0° slowly deposited a precipitate.

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(10) Francimont and Klobbie. *Rec. trav. chim.*, **7**, 17 (1888).

(11) Curtius and Hechtenberg, *J. prakt. Chem.*, **105**, 316 (1922).

(12) Franchimont and Dubsky, *Rec. trav. chim.*, **30**, 84 (1911).

After fifteen minutes the drowned mixture was filtered and the solid was purified by solution in aqueous sodium hydroxide and reprecipitation of the **3,3'-dinitro-1,1'-ethylenebisurea (VI)** as colorless needles; yield, 0.67 g.; m. p. 197–198° dec. The compound is practically insoluble in the common organic solvents.

Anal. Calcd. for $C_4H_8N_6O_6$: C, 20.3; H, 3.4. Found: C, 19.7; H, 3.4.

The dinitrate salt of ethylenebisurea was obtained by adding 200 cc. of nitric acid (d. 1.42) to a solution of 60 g. of ethylenebisurea in 200 cc. of water and cooling; weight, 94.4 g. (92%); m. p. 150–151°. Addition of 13.6 g. of the dinitrate salt with stirring to 43.2 cc. of concentrated sulfuric acid at −5° and drowning after thirty minutes gave 5 g. of dinitro compound with m. p. 180–182°; after solution in alkali, the product melted at 190–192°. A mixture of 1.36 g. of the dinitrate salt and 5 cc. of acetic anhydride, which was warmed on a steam-bath for fifteen minutes, gave 0.56 g. (m. p. 183–185°) of the dinitro compound; after treatment with alkali, the product (0.4 g.) had m. p. 196–197°.

Reactions of 3,3'-Dinitro-1,1'-ethylenebisurea.—A solution of 2 g. of the dinitro compound in 60 cc. of concentrated aqueous ammonia was refluxed for one hour. Evaporation of the solution and recrystallization of the residue from aqueous alcohol gave ethylenebisurea; m. p. 191–192° alone and when mixed with an authentic specimen.

When a mixture of 2.36 g. of the dinitro compound, 3 g. of aniline and 30 cc. of water was refluxed for one hour 1.5 g. of 3,3'-diphenyl-1,1'-ethylenebisurea precipitated; after recrystallization it melted at 246–246.5° alone and when mixed with a sample prepared from anhydrous ethylenediamine and phenyl isocyanate.[11]

Methylolation of EDNA with Formaldehyde.—In an attempt to prepare an explosive polymer 10 g. of powdered EDNA, 8 g. of polyoxymethylene and 1 g. of potassium carbonate in 100 cc. of 95% ethanol was refluxed for one hour. The filtered solution was concentrated to a small volume, and the residue, which crystallized on scratching, was filtered and washed with alcohol; weight, 10.1 g.; m. p. 110–125°. When recrystallized from water containing formalin it formed colorless diamond-shaped crystals, m. p. 124–126°. The same compound was formed by recrystallization of EDNA from water containing formalin. When heated alone the compound is decomposed to EDNA. It was shown later by Dr. G. F Wright that the compound is the monomethylol derivative, $NO_2NHCH_2CH_2N(NO_2)$-CH_2OH.

Summary

The preparation and nitration of 2-imidazolidone, ethylenebisurethan, ethylenebisacetamide and cyclic ethyleneoxamide to dinitro derivatives and the hydrolysis of the dinitro derivatives to the high explosive ethylenedinitramine (EDNA) are described.

Ethylenebisurea, which was prepared from ethylenediamine and urea, is nitrated at the terminal amino groups.

In two instances a mixture of acetic anhydride and 98% nitric acid was able to nitrate compounds which remained unchanged in 98% nitric acid alone or mixed with concentrated sulfuric acid.

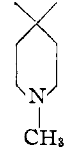
Ann Arbor, Michigan Received January 13, 1950

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

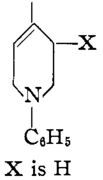
Piperidine Derivatives. XXIII. Certain Halogenated 1-Methyl-4-Phenylpiperidines and Related Compounds

By S. M. McElvain and John C. Safranski, Jr.

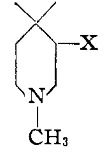
This paper reports the preparation and properties of some halogeno and hydroxy derivatives of 1-methyl-4-phenyl-piperidine and tetrahydropyridine (II–VIII), which were obtained from 1-methyl-4-phenyl-4-hydroxypiperidine (I). The action of thionyl chloride on the hydrochloride of I produced an inseparable mixture of the hydrochlorides of 1-methyl-4-phenyl-4-chloropiperidine (II) and 1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine (IV). The chlorine content of this mixture indicated that it contained approximately 70% of II; its composition was further shown by the fact that an aqueous potassium hydroxide solution or ethylmagnesium bromide in ether converted it to the tetrahydropyridine IV. In contrast to these complete dehydrohalogenations, the 4-chloro component of this mixture was dehydrohalogenated only to the extent of 25% when an ether solution of the mixture was refluxed for two hours.



I, X is OH
II, X is Cl
III, X is Br



IV, X is H
V, X is OH
VI, X is Br



VII, X is Br
VIII, X is OH

A salt of the tetrahydropyridine IV was obtained when the carbinol I was heated with concentrated hydrochloric or hydrobromic acid. The hydrobromide of IV added hydrogen bromide in glacial acetic acid solution to form the hydrobromide of III. Although the latter compound was obtained in 95% purity from this reaction, all attempts to purify it further by recrystallization caused extensive dehydrobromination.

From the addition of bromine to the hydrobromide of IV the two racemic forms of 1-methyl-3,4-dibromo-4-phenylpiperidine (VII) hydrobromide were isolated. Analysis of this salt by the Volhard procedure (an acid solution) gave values indicating that two of the bromines had been titrated, while the analysis by the Mohr procedure (basic solution) gave values corresponding to the titration of all three of the bromines present in this salt. After these results in the Mohr titration, it was not surprising to find that an aqueous solution of sodium cyanide or potas-