[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Linear Secondary Polynitramides (Polynitramines)

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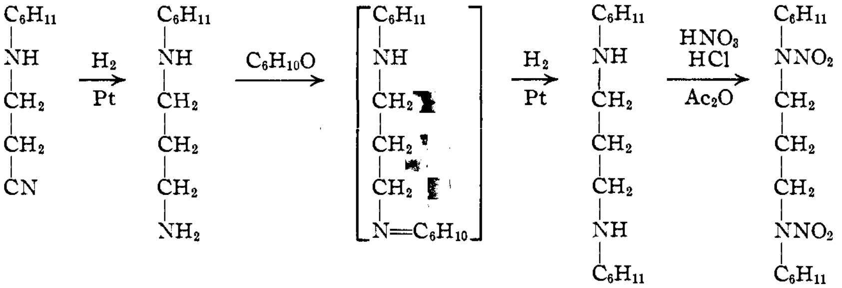
Linear secondary polymethylene nitramides (nitramines) have been prepared by tertiary amine nitrolyses[1,2] and a polyethylenenitramine has been prepared from the corresponding chloramine[3] but the direct nitration of polyamines has not been reported heretofore. The peculiarities of these direct nitrations are outlined in the present paper.

The terminal group chosen for a series of polyethyleneamines and for a disubstituted propylenediamine was cyclohexyl because of the ease of preparation. Thus N,N′-dicyclohexyl-1,3-propanediamine (IV) was prepared from the known β-cyclohexylaminopropionitrile[4] (I) by reduction to the primary amine II from which, with cyclohexanone, the ketimine III was formed and reduced *in situ*. By the same method of reductive condensation with cyclohexanone N,N′-dicyclohexyl-1,2-diaminoethane, VI was isolated (as its dinitrate, dihydrochloride or monohydrate) from ethylenediamine. Likewise triethylenetetramine and tetraethylenepentamine could respectively be converted to 1,8-dicyclohexylamino-3,6-diazaoctane, VII, and 1,11-dicyclohexylamino-3,6,9-triazaundecane, VIII, both of which were isolated as the hydrochlorides.



$$C_6H_{11}NHCH_2CH_2CN \xrightarrow[Pt]{H_2} C_6H_{11}NHCH_2CH_2CH_2NH_2 \xrightarrow{C_6H_{10}O} \left[C_6H_{11}NHCH_2CH_2CH_2N{=}C_6H_{10}\right] \xrightarrow[Pt]{H_2} C_6H_{11}NHCH_2CH_2CH_2NHC_6H_{11} \xrightarrow[Ac_2O]{HNO_3,\ HCl} C_6H_{11}N(NO_2)CH_2CH_2CH_2N(NO_2)C_6H_{11}$$

I II III IV V

When only one-tenth equivalent of chloride catalyst was used in the nitration[5] of these amines a complex mixture of products was obtained beside much unchanged amine salt. The nitration of N,N′-dicyclohexyl-1,3-diaminopropane did succeed, however, when the dihydrochloride was used. The dinitramine, V, was a solid melting at 83° which gave an unmistakable Franchimont test for the nitramino linkage.

The nitration of the first, third and fourth members of the dicyclohexylethyleneamine series was more difficult even when the dihydrochloride was used. It was realized finally that this was owing to the insolubility of both the nitric salt and the intermediate and final products of nitration. Reaction was slow, in consequence, and oftentimes the nitration was incomplete because the short-lived electropositive chlorine catalyst was lost to the system as elemental chlorine. For this reason it was often found advisable to "renitrate" the crude product with acetyl chloride catalyst rather than to attempt a purification by crystallization.

Although the insolubility of these dicyclohexylethyleneamines did necessitate long reaction periods with careful avoidance of salt contamination and over-acidity (in order to preserve the catalyst), this insolubility was not wholly disadvantageous. The eventual high purity of 1,11-dicyclohexylamino-3,6,9-trinitro-3,6,9-triazaundecane was evidence that the usual nitration by-products were not formed. Furthermore N,N′-dicyclohexyl-1,2-diacetaminoethane and N,N′-dicyclohexyl-1,2-dinitrosaminoethane were synthesized by orthodox procedures, but neither was found in the product when N,N′-dicyclohexyl-1,2-diaminoethane was nitrated either with much or little catalyst present. This must be owing to the retardation in reaction rate of by-product formation because of insolubility.

Comparison of the nitration products is set out in Table I. It may be seen that the melting point of the polyethylenenitramine series decreases from the first to the fourth member, but they all melt much higher than does the dicyclohexyldinitraminopropane. They are also much less soluble in organic solvents. This may partly account for the fact that they do not give Franchimont tests for the nitramino linkage. Like nitramines in general they are, however, quite stable in hot 70% nitric acid.

Experimental[6]

N,N′-Dicyclohexyl-1,2-diaminoethane Monohydrate, VI.—A solution of 32.2 g. (0.329 mole) of cyclohexanone and 12.9 g. (0.165 mole) of ethylenediamine monohydrate (both freshly distilled) in 200 cc. of absolute alcohol was reduced at 50 lb. hydrogen pressure and 25° with 0.15 g. of platinum oxide. The filtered solution was acidified to *p*H 3 with *concd.* hydrochloric acid. The 86% yield of crude hydrochloride melted at 311–318°. Crystallization

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(1) A. F. McKay, H. H. Richmond and G. F Wright, *Can. J. Research*, **27B**, 462 (1949).

(2) W. J. Chute, *et al.*, *ibid.*, **27B**, 503 (1949).

(3) G. N. R. Smart and G. F Wright, THIS JOURNAL, **70**, 3141 (1948).

(4) F. C. Whitmore, *et al.*, *ibid.*, **66**, 725 (1944).

(5) W. J. Chute, *et al.*, *Can. J. Research*, **26B**, 114 (1948).

(6) All melting points have been corrected against known standards.

Table I

Yields and Properties of Polynitramines

Amine	Product	Yield, %	N–NO₂ test	M. p., °C.	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
VI	$C_6H_{11}NNO_2CH_2CH_2NNO_2C_6H_{11}$	89	–	212–213	53.9	53.5	8.38	8.78	17.8	18.0
VII	$C_6H_{11}(NNO_2CH_2CH_2)_3NNO_2C_6H_{11}$	94	–	208.6–209.3	44.1	44.3	6.93	6.69	22.8	22.6
VIII	$C_6H_{11}(NNO_2CH_2CH_2)_4NNO_2C_6H_{11}$	81	–	181.3–181.9	41.6	41.5	6.59	6.45	24.2	24.4
IV	$C_6H_{11}NNO_2CH_2CH_2CH_2NNO_2C_6H_{11}$	96	+	83.5–84.1	54.9	55.0	8.63	8.61	17.1	16.9

from water raised this melting point to 322–328°. This hydrochloride was converted by alkali to the free base monohydrate, m. p. 86–93.5°. This indefinite melting point could not be raised by crystallization from 1:1 water–ethanol. This material was partly dehydrated during distillation at 177–178° at 18 mm., but the semi-solid distillate soon solidified on exposure to atmospheric moisture. *Anal.* Calcd. for $C_{14}H_{30}N_2O$: C, 69.3; H, 12.5; N, 11.5. Found: C, 69.0; H, 12.3; N, 11.4.

The nitric salt of this diamine could be prepared by addition of 70% nitric acid to its cold ether solution. After crystallization from water (3 g. per 100 ml. at 25°, 13 g. per 100 ml. at 80°) the salt melted at 190–192°. *Anal.* Calcd. for $C_{14}H_{30}N_4O_6$: C, 47.9; H, 8.64; N, 16.0. Found: C, 48.2; H, 8.81; N, 15.6.

This salt was also obtained, in 30% yield, when 1.18 g. (0.005 mole) of 1,3-dicyclohexylimidazolidine was treated with 4 equivalents of ammonium nitrate and 8 equivalents of acetic anhydride in 5 cc. of acetic acid at 65–73° over three minutes. After two hours at 65° the mixture, diluted into 10 cc. of water, yielded 0.5 g. of dinitrate, m. p. 187–188°. The remainder of the diamine could be recovered from the liquors by neutralization.

A slightly higher yield of the nitrate salt (0.68 g., 40%) was obtained when a chloroform solution of dicyclohexylimidazolidine at 0° was treated with 20 equivalents of 95% nitric acid and then poured into ice.

N,N′-Dicyclohexyl-1,2-diacetaminoethane.—A solution of 4.96 g. (0.02 mole) of N,N′-dicyclohexyl-1,2-diaminoethane monohydrate, I, in 24 cc. (0.25 mole) of acetic anhydride was boiled under reflux for one hour. After addition of 5 cc. of water the acetic acid was distilled off under 20 mm. to leave a white solid, m. p. 150–152°. After crystallization from acetone this weighed 3.1 g. (52%) and melted at 151–152°. *Anal.* Calcd. for $C_{18}H_{32}N_2O_2$: C, 70.1; H, 10.4; N, 9.1. Found: C, 69.6; H, 10.0; N, 9.2.

N,N′-Dicyclohexyl-1,2-dinitrosaminoethane.—A solution of 7.8 g. (0.021 mole) of N,N′-dicyclohexyl-1,2-diaminoethane dinitrate in 250 cc. of water was stirred at 25° while 5.55 ml. (0.09 mole) of 70% nitric acid and a saturated solution of 10.3 g. (0.05 mole) of sodium nitrite in water were added simultaneously; the *p*H was maintained between 2–4. After five hours the excess nitrous acid was destroyed by addition of sulfamic acid. The crude bis-nitrosamine was filtered off. It weighed 5.4 g. (90%) and melted at 143–145°. This was crystallized from nitromethane, ethyl acetate, absolute ethanol, absolute acetone, pet. ether (b. p. 90–100°). It then melted at 144.3–144.6°. *Anal.* Calcd. for $C_{16}H_{24}N_4O_2$: C, 59.5; H, 9.3; N, 19.8. Found: C, 59.9; H, 9.2; N, 20.0.

The compound gave a positive Liebermann and a negative Franchimont test. Attempts to oxidize it to the bis-nitramine over the temperature range −50 to +50° with ammonium persulfate in 99% nitric acid[7] yielded either unchanged bis-nitrosamine or adipic acid.

N,N′-Dicyclohexyl-1,2-dinitraminoethane.—To 4.2 ml. (0.1 mole) of 99% nitric acid at 0° was slowly added 14.6 ml. (0.15 mole) of acetic anhydride in 20 cc. of acetic acid. To this solution was then added 3 g. (0.01 mole) of N,N′-dicyclohexyl-1,2-diaminoethane dihydrochloride. After two hours from 0 to 25° and twenty hours at the latter temperature the original slurry seemed to dissolve, but produced a new solid. This new slurry was partly evaporated at 20 mm., then heated to 60–70° at atmospheric pressure, and finally evaporated to dryness at 20 mm. The residue was boiled with 50 cc. of water. The suspension was filtered to yield 2.8 g. of crude nitramine, m. p. 202–203° (soft at 171°). This material (89% of theoretical) was only slightly contaminated with halogen. It was crystallized from 4.3 cc. of 70% nitric acid (m. p. 211–212°), then from 8 cc. of isopropyl ether and finally from 1.3 cc. of pyridine to melt at 212–213°. It could also be crystallized from chloroform (20 cc. per gram), chloroform–petroleum ether or 1:6 benzene–petroleum ether (b. p. 60–70°).

1,8-Dicyclohexylamino-3,6-diazaoctane Tetrahydrochloride VII. A. From Ethanol Medium.—A solution of 3.94 g. (0.0403 mole) of distilled cyclohexanone and 2.95 g. (0.0202 mole) of distilled triethylenetetramine in 25 cc. of abs. ethanol was reduced at room temperature over two to five hours with hydrogen (20–30-lb. gage) and 0.02 g. of platinum oxide. The filtered solution (clarified when necessary with "Filtercel") was acidified to *p*H 4 with concd. hydrochloric acid and was then evaporated *in vacuo* to leave 8.0 g. or 87% of the expected amount of product, m. p. 290°. This was not pure since the apparent hydrogen chloride content was 4.2 moles rather than the 4 moles expected for this product. Purification consisted in threefold crystallization from water at 25° by addition of concd. hydrochloric acid. It then melted at 299.4–299.7° and precipitated the silver halide expected for the tetrahydrochloride. *Anal.* Calcd. for $C_{18}H_{42}N_4Cl_4$: C, 47.4; H, 9.23; N, 12.3. Found: C, 47.9; H, 9.27; N, 12.5. The free base (or its hydrate), m. p. 73–75°, has not been freed from the sodium chloride formed during its precipitation from the aqueous hydrochloride solution by alkali.

B. From Aqueous Medium.—When cyclohexanone and triethylenetetramine were reduced in 25 cc. of water rather than the same quantity of ethanol a white solid precipitated during reduction. Addition of 12 cc. of ethanol dissolved the precipitate so that the catalyst could be filtered off. Evaporation of the acidified solution left 6.9 g. of solid, m. p. about 280° which, however, had an apparent hydrochloride content of 4.8 equivalents per mole.

1,8-Dicyclohexylnitramino-3,6-dinitro-3,6-diazaoctane.—To a solution of 4.4 ml. (0.1 mole) of 95% nitric acid in 15.0 ml. (0.16 mole) of acetic anhydride and 20 ml. of acetic acid at 1° was added 4.56 g. (0.01 mole) of crude 1,8-dicyclohexylamino-3,6-diazaoctane. The temperature was raised to 20–25° after thirty minutes and the slurry was stirred at this temperature for forty-four hours. After evaporation under reduced pressure, finally at 70°, the residual solid was boiled in 75 cc. of water for an hour. Hot filtration of the suspension yielded 4.65 g. (94%) of the crude nitramine, m. p. 200–204°. This melting point was raised to 207.7–208° by crystallization, with 10% loss, from 50 cc. of boiling 70% nitric acid and then from hot pyridine (10 cc. per g.) to melt at 208.6–209.3°. This dicyclohexyltriethylenetetranitramine gave negative Beilstein, Liebermann and Franchimont tests for halogen, nitrosamine and nitramine, respectively. It could be detonated with great difficulty by a glancing blow between medium-hard steel surfaces.

1,11-Dicyclohexylamino-3,6,9-triazaundecane Pentahydrochloride VIII.—A solution of 3.94 g. (0.0403 mole) of distilled cyclohexanone and 3.82 g. (0.0202 mole) of distilled tetraethylenepentamine in 25 cc. of absolute ethanol was reduced and processed subsequently as described above to yield 9.7 g., m. p. 274–276° (90%), of the crude pen-

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(7) W. J. Chute, *et al.*, *Can. J. Research*, **26B**, 89 (1948).

tahydrochloride of dicyclohexyltetraethylenepentamine. This crude product had an apparent content of 5.5 equivalents of hydrogen chloride. It was thrice purified by solution in a minimum of water from which it was precipitated by addition of concd. hydrochloric acid. It then melted at 278.6–279.1° with decomposition, but it softened at 275°. Analysis by silver halide precipitation then indicated that it contained 5 equivalents of hydrogen chloride per mole. *Anal.* Calcd. for $C_{20}H_{43}N_5Cl_5$: C, 44.8; H, 9.04; N, 13.1. Found: C, 45.4; H, 8.98; N, 13.2.

The free base, or its hydrate, m. p. 59–61°, has not been freed from sodium chloride formed by treatment of the hydrochloride with aqueous alkali.

1,11-Dicyclohexylnitramino-3,6,9-trinitro-3,6,9-triazaundecane.—To a solution of 13.2 ml. (0.30 mole) of 95% nitric acid in 30 ml. (0.32 mole) of acetic anhydride and 40 ml. of acetic acid, prepared at 1°, was added 10.9 g. (0.02 mole) of crude 1,11-dicyclohexylamino-3,6,9-triazaundecane pentahydrochloride. After seventy-two hours at 20–25° the slurry was evaporated *in vacuo*, finally at 70°. The residue was boiled an hour with 300 cc. of water. The dull-white solid weighed 9.4 g. (81%); it melted at 165–168° with decomposition but softened at 155°. Two crystallizations from 30 and then 20 cc. of boiling 70% nitric acid raised the melting point to 170–174°. Crystallization from boiling pyridine raised the melting point only slightly, but when the 1.15 g. (0.002 mole) of the material was renitrated with 0.44 ml. (0.01 mole) of 95% nitric acid and 0.3 ml. (0.004 mole) of acetyl chloride in 1.1 ml. (0.012 mole) of acetic anhydride the product, melting at 173–174°, was purified easily from boiling pyridine (10 cc. per g.) to melt at 181.3–181.9°. The compound gave negative Beilstein, Liebermann, Franchimont and Brucine tests for halogen, nitrosamine, nitramine and nitrate, respectively.

β-Cyclohexylaminopropionitrile I.—A solution of 80 g. (0.8 mole) of cyclohexylamine in 200 cc. of ethanol was stirred at 15° while 2.9 g. (0.55 mole) of acrylonitrile in 20 cc. of ethanol was added over a twenty-minute period. After five more hours at this temperature the solution was boiled under reflux for an hour. After distillation of the alcohol, followed by a first fraction (26.9 g.) boiling up to 80° (3 mm.) the main fraction (76.2 g.) was distilled at 80–130° (3 mm.). This main fraction was redistilled at 115–117° (6 mm.). It weighed 66 g. or 64%.

N-Cyclohexyl-N-phenylthiocarbamyl-β-aminopropionitrile.—Two grams of phenyl isothiocyanate was added to 2 g. of β-cyclohexylaminopropionitrile and shaken for two minutes. The hot yellow solution was cooled in an ice-bath. The precipitated yellow glass was ground up, washed with petroleum ether (b. p. 90–100°), then recrystallized from petroleum ether (b. p. 60–70°), 95% ethyl alcohol, acetone, ethyl acetate, benzene, acetone-water (1:1) and chloroform. It then melted at 124°. *Anal.* Calcd. for $C_{16}H_{21}N_3S$: C, 66.8; H, 7.37; N, 14.6; S, 11.1. Found: C, 66.3; H, 7.28; N, 15.0; S, 10.9.

N-Cyclohexyl-1,3-propanediamine, II.—A solution of 15.2 g. (0.10 mole) of cyclohexylaminopropionitrile[10,8] in 112 g. of methanol containing 4.3 g. (0.25 mole) of anhydrous ammonia was hydrogenated with 9 g. of Raney nickel at 2000 lb. and 140° over twelve hours. The nickel was filtered off, and the filtrate evaporated at 25° (30 mm.) to leave a green oil which distilled at 120–135° (17 mm.). It weighed 13 g. or 83%. On redistillation this boiled at 120–123° (20 mm.).

N-Cyclohexyl-N'-phenylthiocarbamyl-1,3-propanediamine.—This preparation and purification, identical with that of N-cyclohexyl-N-phenylthiocarbamyl-β-aminopropionitrile yielded a product melting at 138.5°. *Anal.* Calcd. for $C_{16}H_{23}N_3S$: C, 65.9; H, 8.65; N, 14.4; S, 11.0. Found: C, 65.2; H, 8.78; N, 14.7; S, 11.2.

N,N'-Dicyclohexyl-1,3-propanediamine, IV.—A solution of 14.5 g. (0.093 mole) of N-cyclohexyl-1,3-propanediamine and 9.6 ml. (0.093 mole) of pure cyclohexanone in 100 cc. of absolute ethanol was reduced with 0.2 g. of platinum oxide catalyst at 24° (60 lb. initial pressure) over four hours. The filtered solution was treated overnight with 50 ml. of concd. hydrochloric acid. The fine white crystalline hydrochloride which separated was filtered and washed with ethanol. It weighed 26.0 g. (91%). After solution in 60 ml. of hot water this could be converted to the oily free base by addition of alkali. The solidified oil melted at 30–32° and could be crystallized from petroleum ether (b. p. 60–70°) or ethanol to melt at 33°. *Anal.* Calcd. for $C_{15}H_{30}N_2$: C, 75.5; H, 12.7; N, 11.2. Found: C, 74.4; H, 12.6; N, 11.0.

The compound formed a dipicrate which crystallized from ethanol and melted at 237–237.5°. *Anal.* Calcd. for $C_{27}H_{36}N_8O_{14}$: C, 47.3; H, 5.30; N, 16.3. Found: C, 47.1; H, 5.40; N, 16. 5.

N,N'-Dicyclohexyl-1,3-dinitraminopropane V.—A solution was prepared at 0° by addition of 20 ml. of acetic acid and 14.6 ml. (0.15 mole) of acetic anhydride in that order to 4.2 ml. (0.1 mole) of 99% nitric acid. To this solution was added at once 3.1 g. (0.01 mole) of bis-cyclohexylpropylenediamine dihydrochloride. After twenty hours, chiefly at room temperature, the slurry had dissolved. The solution was distilled with bath temperature 60° (20 mm.) and the residue treated with 30 cc. of water. An oil separated which melted after solidification at 67–70°, and weighed 3.15 g. (96%). This compound was insoluble in ether but soluble in cold acetone and hot chloroform or ethanol. It was crystallized from absolute ethanol to yield 1.65 g., m. p. 80–81°. Repeated recrystallization from the same solvent raised the melting point to 83.5–84.1°. The compound gave a positive Franchimont test for a nitramine.

Summary

1. Cyclohexanone reacts smoothly with N-cyclohexyl-1,3-diaminopropane, ethylenediamine, triethylenetetramine and tetraethylenepentamine to give substituted ketimines that may be reduced *in situ* to the secondary amines.

2. These secondary amines can be nitrated if much electropositive chlorine catalyst is present, but the insolubility of the initial and intermediate salts makes nitration slow and renitration frequently necessary.

3. The dicyclohexylethylenepolynitramides (polynitramines) are high melting, highly insoluble solids which do not respond to the Franchimont test for the nitramino group.

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