Anal. Calcd. for $C_{22}H_{36}O_3N_2$: C, 70.16; H, 9.64; N, 7.45. Found: C, 70.66; H, 9.53; N, 7.18.

N-(2,2-Dibutylhexyl)-2-carboxynicotinamide (12).—A solution of 5.5 g. of N-(2,2-dibutylhexyl)-2-carbomethoxynicotinamide, 3 g. of sodium hydroxide, 40 cc. of ethanol and 10 cc. of water was allowed to stand for three hours at room temperature. The solution was poured into cold water and acidified with dilute hydrochloric acid. The tan, amorphous solid (5.2 g.) which separated was dried and recrystallized from a mixture of chloroform-petroleum ether from which it separated as a white crystalline solid; yield 2.8 g. (53%), m. p. 128–129°.

Anal. Calcd. for $C_{21}H_{34}O_3N_2$: N, 7.73. Found: N, 8.20.

Decarboxylation of N-(2,2-Dibutylhexyl)-2-carboxynicotinamide.—One gram of N-(2,2-dibutylhexyl)-2-carboxynicotinamide was heated for forty minutes at 140°. The residue was cooled and dissolved in a mixture of alcohol and water. The white precipitate which separated was filtered, washed with sodium carbonate solution, water and dried. The solid was recrystallized from a mixture of alcohol and water, m. p. 104–105, mixed m. p. with N-(2,2-dibutylhexyl)-nicotinamide (VII), 104–105°.

N-(2,2-Dibutylhexyl)-1-methylnipecotamide (VIII) (13).—A solution of 23.3 g. (0.063 mole) of N-(2,2-dibutylhexyl)-nicotinamide in 350 cc. of methanol was reduced with Raney nickel catalyst at an initial pressure of 1,500 lb. for ten hours at 170°. After removal of the catalyst and the solvent, a cloudy oil remained which was dissolved in ether, the ether solution dried and then distilled. The residue (23 g.) was a waxy, amorphous solid melting at 68–69°. The hydrochloride was prepared in the usual manner and melted at 168–169° after a recrystallization from alcohol-ether.

Anal. Calcd. for $C_{21}H_{43}ON_2Cl$: C, 67.24; H, 11.55; N, 7.47. Found: C, 66.68; H, 11.30; N, 7.52.

VIII formed a picrate after standing for three days, m. p. 129–130°. The methiodide, m. p. 231–232°, could not be recrystallized satisfactorily for analysis. The methylation of the piperidine nitrogen was indicated by the fact that no heat was evolved when VIII was treated with pyridine and acetic anhydride.

N-(2,2-Dibutylhexyl)-nipecotamide (IX).—A solution of 31.8 g. of N-(2,2-dibutylhexyl)-nicotinamide in 350 cc. of dioxane was reduced with Raney nickel catalyst at an initial pressure of 1,000 lb. at 165°. The catalyst and solvents were removed and the black, viscous residue distilled; yield 22 g., b. p. 212–214° (3.5 mm.), m. p. 70–72°. Attempts to recrystallize the product were unsuccessful. The following analysis was made on the liquid sample.

Anal. Calcd. for $C_{20}H_{40}ON_2$: C, 74.01; H, 12.43; N, 8.64. Found: C, 74.19; H, 12.57; N, 8.48.

A mixed melting point of VIII (m. p. 68–69°) and IX (m. p. 70–72°) was depressed (54–56°).

IX gave a gummy hydrochloride and picrate. When IX was treated with acetic anhydride and pyridine, considerable heat was evolved and an oily precipitate resulted when the solution was poured on ice.

N-(2,2-Dibutylhexyl)-1-methylnipecotamide (VIII) by the Methylation of IX.—To 15 g. (0.0463 mole) of IX was added with cooling 12.0 g. of 90% formic acid followed by 10.5 cc. of 37% formaldehyde solution.[10] The flask was heated on the steam-bath and carbon dioxide was evolved rapidly. After twelve hours, the viscous liquid was basified with sodium hydroxide pellets and the oily solid taken up in ether. The ether layer was washed with water, dried, the ether distilled and the oily residue fractionated; yield 14 g. (90%), b. p. 188–190° (1 mm.), colorless oil which crystallized slowly, m. p. 64–65°, mixed m. p. with a sample of VIII prepared by the reduction of VII in methanol (m. p. 68–68°) showed no depression (m. p. 65–66°).

Anal. Calcd. for $C_{21}H_{42}ON_2$: C, 74.47; H, 12.51; N, 8.28. Found: C, 74.50; H, 12.59; N, 8.23.

The methiodide of VIII (m. p. 228–229°), prepared from IX, did not depress the melting point of the methiodide (m. p. 231–232°) prepared by the reduction of VII in methanol (mixed m. p. 229–229.5°).

Acknowledgment.—The authors wish to express their appreciation to Mrs. Rosemarie Fricano for her assistance and to Dr. Richard Tislow and Mrs. Annette LaBelle for the pharmacological data reported herein.

Summary

A series of N-trisubstituted alkyl pyridine carboxamides has been prepared and tested for antispasmodic activity. N-(2,2-Dibutylhexyl)-nicotinamide was the most potent member of the series. The carboxy substituted and the N-methyl hydrogenated derivative of N-(2,2-dibutylhexyl)-nicotinamide have been synthesized.

BLOOMFIELD, NEW JERSEY RECEIVED OCTOBER 13, 1949

[CONTRIBUTION FROM THE INORGANIC CHEMISTRY BRANCH, CHEMISTRY DIVISION, RESEARCH DEPARTMENT, U. S. NAVAL ORDNANCE TEST STATION]

The Hydrazinolysis of Nitroguanidine and Alkylnitroguanidines[1]

BY RONALD A. HENRY, HENRY D. LEWIS AND G. B. L. SMITH

Phillips and Williams[2] first prepared nitroaminoguanidine, $NH_2NHC(NH)NHNO_2$, in low yield[3] by the hydrazinolysis of nitroguanidine in aqueous solutions. Attempts by these workers to isolate and identify the products of the side-reactions which were decreasing the yield were only partially successful; they showed that nitrous oxide was evolved in an amount corresponding to a loss of approximately one-half of the nitroguanidine.

A satisfactory prediction of the by-products in this reaction can be made, based upon previous studies by Davis and co-workers.[4] They have shown that monoalkylamines react with nitroguanidine in aqueous solution to give the corre-

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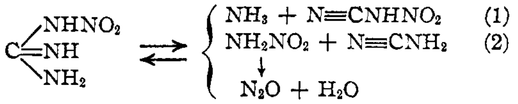
(1) Part of the material presented in this paper was abstracted from the B.S. thesis of Henry D. Lewis, Polytechnic Institute of Brooklyn, June 1942.

(2) Phillips and Williams, THIS JOURNAL, **50**, 2465 (1928).

(3) Phillips and Williams stated that their yields were about 50%; repeated duplication of their work, together with more precise methods for the analysis of nitroaminoguanidine in the crude products, indicated that the yields were actually only 30–35%.

(4) Davis and Abrams, *Proc. Am. Acad. Arts and Sciences*, **61**, 437 (1926); Davis and Elderfield, THIS JOURNAL, **55**, 731 (1933); Davis and Luce, *ibid.*, **49**, 2303 (1927). The use of the Davis dearrangement mechanism in this paper is schematic only and should not be taken to mean that this is the actual or sole mechanism involved.

sponding 1-alkyl-3-nitroguanidine and alkylguanidine. The alkylnitroguanidine in turn reacts with excess alkylamine to form, among other things, 1,3-dialkylguanidine. If hydrazine can be considered to react analogously to a monoalkylamine (NH_2- instead of R-) then the expected products should be nitroaminoguanidine, aminoguanidine, and diaminoguanidine. In addition to its formation by reaction 6, diaminoguanidine could also arise from the hydrazinolysis[5] of the aminoguanidine formed by reaction 4.



$$\mathrm{C}\begin{cases}\mathrm{NHNO_2}\\ \mathrm{=NH}\\ \mathrm{NH_2}\end{cases} \rightleftarrows \begin{cases} \mathrm{NH_3 + N{\equiv}CNHNO_2} & (1)\\ \mathrm{NH_2NO_2 + N{\equiv}CNH_2} & (2)\\ \quad\downarrow & \\ \mathrm{N_2O + H_2O} & \end{cases}$$

$$\mathrm{N{\equiv}CNHNO_2 + NH_2NH_2 \rightleftarrows NH_2NHC(NH)NHNO_2} \quad (3)$$

$$\mathrm{N{\equiv}CNH_2 + NH_2NH_2 \rightleftarrows NH_2NHC(NH)NH_2} \quad (4)$$

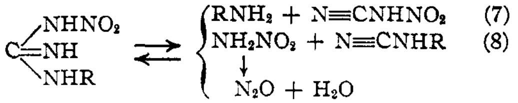
$$\mathrm{NH_2NHC(NH)NHNO_2 \rightleftarrows NH_2NO_2 + N{\equiv}CNHNH_2} \quad (5)$$
$$\downarrow$$
$$\mathrm{N_2O + H_2O}$$

$$\mathrm{N{\equiv}CNHNH_2 + NH_2NH_2 \rightleftarrows NH_2NHC(NH)NHNH_2} \quad (6)$$

The method used to separate and isolate the by-products with hydrazino groups remaining in the mother liquors after the nitroaminoguanidine had been recovered from a typical preparation, consisted of forming in nitric acid solution, the sparingly soluble benzaldehyde hydrazones which were fractionally crystallized. When pure samples were obtained, the materials were identified. The two principal products isolated and identified were derivatives of the predicted amino- and diaminoguanidine. Although the fractional crystallizations and purifications made the determination of percentage yield rather difficult, it is estimated that approximately twice as much diaminoguanidine on a weight basis was produced as aminoguanidine when equivalent quantities of the hydrazine and nitroguanidine reacted. A third benzaldehyde hydrazone was also isolated in small yield but was not identified. No derivatives of triaminoguanidine were recovered although triaminoguanidine could have been formed by the further hydrazinolysis of diaminoguanidine.[5]

The reaction of hydrazine with nitroaminoguanidine (equations 5 and 6) in aqueous solutions has been separately demonstrated to proceed under the same conditions as employed for the nitroguanidine–hydrazine reaction, to yield diaminoguanidine, and to reach completion in about the same length of time. This consecutive reaction probably competes very strongly with the concurrent reaction that leads to aminoguanidine in decreasing the over-all conversion of nitroguanidine to nitroaminoguanidine.

The reaction of hydrazine with alkylnitroguanidines has not been reported previously. Since alkylnitroguanidines are capable of dearrangement in two modes,[4] the expected reactions can be represented schematically as



$$\mathrm{C}\begin{cases}\mathrm{NHNO_2}\\ \mathrm{=NH}\\ \mathrm{NHR}\end{cases} \rightleftarrows \begin{cases} \mathrm{RNH_2 + N{\equiv}CNHNO_2} & (7)\\ \mathrm{NH_2NO_2 + N{\equiv}CNHR} & (8)\\ \quad\downarrow & \\ \mathrm{N_2O + H_2O} & \end{cases}$$

$$\mathrm{N{\equiv}C{-}NHNO_2 + N_2H_4 \rightleftarrows NH_2NHC(NH)NHNO_2} \quad (9)$$

$$\mathrm{N{\equiv}C{-}NHR + N_2H_4 \rightleftarrows NH_2NHC(NH)NHR} \quad (10)$$

Both the nitroaminoguanidine and the alkylaminoguanidine can undergo further hydrazinolysis, yielding diaminoguanidine.

Nitroaminoguanidine, diaminoguanidine and butylamine have been identified as the products of the hydrazinolysis of 1-*n*-butyl-3-nitroguanidine in aqueous solutions; no 1-*n*-butyl-3-aminoguanidine was detected. However, when this same hydrazinolysis was performed in ethyl alcohol, the principal products were 1-*n*-butyl-3-aminoguanidine and diaminoguanidine. Semi-quantitatively it has been observed that the rate of hydrazinolysis of *n*-butylnitroguanidine is considerably slower than that of nitroguanidine under the same conditions.

Experimental[6]

Isolation and Identification of the By-products Formed in the Hydrazinolysis of Nitroguanidine in Aqueous Systems.—Hydrazine sulfate (0.5 mole) and nitroguanidine (0.5 mole) were treated according to the procedure of Phillips and Williams.[2] The resulting solution was neutralized with concentrated hydrochloric acid, evaporated to 300 ml. and chilled overnight at 0°. After the precipitated nitroaminoguanidine and unchanged nitroguanidine were removed by filtration, the mother liquor was acidified with 25 ml. of concentrated nitric acid and shaken vigorously with 30 ml. of benzaldehyde. When the precipitation of the hydrazones was complete (aided by cooling in an ice-bath), they were removed by filtration and washed with cold water until essentially free of acid. The still wet hydrazones were extracted with diethyl ether to remove the unreacted benzaldehyde and any benzalazine that was formed from uncondensed hydrazine. The yield of the azine varied from 2 to 8 g. in several experiments. Based on these quantities, 1.5 to 6.5% of the free hydrazine was not consumed in the hydrazinolysis. The weight of crude, dried hydrazones varied from 30 to 40 g.

The following procedure is typical of the method used to fractionate and identify these crude benzal hydrazones.

Step A.—A solution of 58.9 g. of the hydrazones in 600 ml. of boiling 95% ethyl alcohol was poured with stirring into 1500 ml. of water at 75°. Heating at 75–80° for five minutes usually served to dissolve any material that might have separated during the mixing. This solution was slowly cooled to 40°; the crystalline material was removed by filtration and washed once with a cold solution of 20 ml. of ethyl alcohol in 60 ml. of water. The yield of air-dried product, m. p. 160–170°, was 29.8 g. When this fraction was recrystallized from 500 ml. of 95% ethyl alcohol, the major portion was recovered as a felt-like mass of fine, white needles, m. p. 201–203°. After a second recrystallization, the m. p. was 203–204°. A mixed m. p. with an authentic sample of dibenzaldiaminoguanidine nitrate showed no depression.

In some experiments, a part of the diaminoguanidine was recovered as the dibenzaldiaminoguanidine sulfate,

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[5] Pellizzari and Gaiter, *Gazz. chim. ital.*, **44**, II, 78 (1914).

[6] All melting points are uncorrected.

m. p. 222–223° (dec.), crystallizing from 95% ethyl alcohol, in which it is only sparingly soluble, as a white granular powder.

Anal. Calcd. for $(C_{15}H_{15}N_5)_2 \cdot H_2SO_4 \cdot 2H_2O$: C, 54.20; H, 5.46; N, 21.07; H_2O, 5.42; SO_4^{++}, 14.44. Found: C, 54.46, 54.05, 54.42; H, 5.17, 5.41; N, 21.10, 21.20; H_2O, 5.9, 6.1; SO_4^{++}, 14.10.

This compound formed a picrate, m. p. 240–241° (dec.), identical with the one obtained from dibenzaldiaminoguanidine nitrate.

Step B.—The mother liquor and washings from Step A were heated to boiling in order to re-dissolve any solid material that might have separated. Cooling at 0° for 60 hours yielded 3.8 g. of solid, m. p. 145–150°. By extraction with 300 ml. of boiling water, 1.7 g. more of crude dibenzaldiaminoguanidine nitrate were recovered from this solid. Two recrystallizations of the water-insoluble fraction from ethyl alcohol gave pale yellow or cream-colored spherulites or rosettes, m. p. 172–173°. This material did not form a picrate; it was analyzed but not identified further.

Anal. Calcd. for $C_{21}H_{22}N_{10}O_4$: C, 52.71; H, 4.63; N, 29.28. Found: C, 52.62, 52.36, 52.57, 52.32; H, 4.72, 4.85, 4.83, 4.70; N, 29.31, 29.40, 29.17.

Step C.—When the original mother liquor from Step B was evaporated to 700 ml. and cooled, 9.0 g. of crystalline material decomposing at 165° was obtained. Further evaporation to 50 ml. gave 8.6 g. additional solid melting at 164–165°. Recrystallization of these crops from either water or alcohol yielded benzalaminoguanidine nitrate, m. p. 170–171°,[7] identical with an authentic sample.

Dibenzaldiaminoguanidine Picrate.—From dibenzaldiaminoguanidine nitrate and picric acid in alcohol, there was obtained a bright yellow crystalline powder, m. p. 241–242° (dec.).

Anal. Calcd. for $C_{15}H_{15}N_5 \cdot C_6H_2(NO_2)_3OH$: N, 22.67. Found: N, 22.67, 22.93, 22.63.

Benzalaminoguanidine Picrate.—A boiling solution of 2.2 g. of picric acid in 100 ml. of a 50–50 water–ethyl alcohol mixture was added to 2.0 g. of benzalaminoguanidine nitrate dissolved in 50 ml. of the aqueous alcohol solvent. The yellow precipitate which appeared immediately was digested for a few minutes, filtered, washed with two 50-ml. portions of boiling solvent and dried; m. p. 254–256° (dec.). The picrate can be recrystallized from aqueous alcohol to furnish orange-yellow clusters of very fine needles; m. p. 254–255° (dec.).

Anal. Calcd. for $C_{14}H_{13}N_7O_7$: C, 42.97; H, 3.35; N, 25.06. Found: C, 43.18; H, 3.41; N, 25.11.

Reaction of Hydrazine Hydrate with Nitroaminoguanidine.—A solution consisting of 11.9 g. of once recrystallized nitroaminoguanidine (0.1 mole), 5.75 g. of 87% hydrazine hydrate (0.1 mole), and 300 ml. of water was heated at 55–60° for ninety minutes until the nitroaminoguanidine had completely dissolved. There was a vigorous evolution of gas during the course of the heating, but it contained only traces of ammonia. After neutralizing with concentrated hydrochloric acid and cooling overnight at 0°, 3.3 g. of unchanged nitroaminoguanidine was recovered. A second crop of 0.5 g. was also obtained upon evaporation to 100 ml. (total recovery was 31.9%). To the filtrate, acidified with 5 ml. of concentrated nitric acid, were added 15 g. of benzaldehyde with shaking. The solid was removed by filtration, washed with water until neutral, and then washed with ether to remove excess benzaldehyde and any benzalazine present. The weight of impure dibenzaldiaminoguanidine nitrate, m. p. 165–175°, was 17.6 g., or 53.7% of theory. Several recrystallizations from alcohol raised the m. p. of the felty needles to 205–206°; mixed m. p. with dibenzaldiaminoguanidine nitrate was 205°. Work-up of the alcoholic recrystallization liquors gave no products other than the dibenzaldiaminoguanidine nitrate.

Reaction of Hydrazine with 1-*n*-Butyl-3-nitroguanidine. A. In Water.—A solution of 8.6 g. of 87% hydrazine hydrate (0.15 mole) in 75 ml. of water was added with stirring to a solution of 24.0 g. of *n*-butylnitroguanidine (0.15 mole) in 150 ml. of water at 55–60° during fifty minutes. Some ammonia was evolved but there was also a very strong odor of butylamine. By stirring for twenty-five minutes more, everything dissolved. After cooling to 35° and neutralizing to *p*H 5 with concentrated hydrochloric acid, a white solid separated which was further increased in amount by chilling in an ice-bath for one-half hour. Filtration and drying gave 12.5 g. of material melting at 80–85°. Recrystallization from ethyl alcohol, in which it is readily soluble, raised the m. p. to 84–85°, identical with that of the starting butylnitroguanidine.

By cooling the mother liquor for two days at 0°, 3.2 g. more of grey-white solid was recovered, m. p. 160–170°. Two extractions with 25-ml. portions of boiling ethyl alcohol removed a trace of butylnitroguanidine and raised the m. p. to 184° (dec.). After recrystallization from water, the m. p. was 188° (dec.); a mixed melting point with nitroaminoguanidine was the same.

Upon evaporation of the mother liquor to 100 ml. and cooling, 1.0 g. more of *n*-butylnitroguanidine (total recovery amounted to 56.3%) and 0.2 g. of nitroaminoguanidine were obtained. The total conversion to nitroaminoguanidine, based on the *n*-butylnitroguanidine consumed, was 44.8%.

The hydrazine compounds remaining in solution were recovered as benzal derivatives. By shaking with 5 ml. of concentrated nitric acid and 20 ml. of benzaldehyde, 23.8 g. of yellow material precipitated; m. p. 88–90° after drying. From this material 15.4 g. of benzalazine was extracted with ether, corresponding to 3.7 g. of unreacted hydrazine hydrate, or 43%. The 8.4 g. of ether insoluble material was fractionally crystallized from 95% ethyl alcohol. The first three crops melted at 208° after recrystallization from alcohol; mixed melting point with dibenzaldiaminoguanidine nitrate was the same. The alcoholic solution remaining after the third crop had been removed by filtration was evaporated to dryness and residue extracted with two 100-ml. portions of boiling water to free it of traces of dibenzaldiaminoguanidine nitrate. Several recrystallizations of the water-insoluble material from alcohol finally gave a product decomposing sharply at 172–173°; mixed melting point with benzalaminoguanidine nitrate was 145°. A mixed melting point with a similar unidentified fraction (B) from the hydrazine–nitroguanidine experiments was 172–173°.

n-Butylamine was isolated and identified as follows: the mother liquors left after the benzal derivatives had been separated were cooled and made alkaline with 12.5 g. of solid sodium hydroxide. When this solution was shaken with 15 g. of *p*-nitrobenzoyl chloride for three hours at 70°, there was obtained 10.2 g. of a product softening at 95–130°. Diethyl ether extraction of this crude solid gave 2.6 g. of soluble material; m. p. 93–96°. One recrystallization from alcohol raised the melting point to 103°; a mixed melting point with an authentic sample of N-(*n*-butyl)-*p*-nitrobenzamide was 103–104°. The ether insoluble was *p*-nitrobenzamide; m. p. 193–195°.

B. In Alcohol.—A solution of 8.93 g. of recrystallized *n*-butylnitroguanidine (0.056 mole) and 3.21 g. of 87% hydrazine hydrate (0.056 mole) in 100 ml. of absolute alcohol was heated for ninety minutes under reflux. Ammonia was evolved and the solution developed a deep yellow color. The odor of butylamine also was evident. No precipitate formed, nor did overnight cooling at 0° induce any crystallization. After evaporating the solution to a small volume under reduced pressure, the oily residue was dissolved in 200 ml. of water, acidified with nitric acid, and treated with 5.9 g. of benzaldehyde. The resulting hydrazones were removed by filtration, washed with water until essentially free of acid, and recrystallized from al-

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[7] In connection with this work, the observation was made that benzalaminoguanidine nitrate can exist in two forms, one melting at 161° in agreement with the literature value (Thiele and Heidenreich, *Ber.*, **26**, 2599 (1893)) and a more stable form melting at 170–171°. Seeding the low melting, metastable form with the high was sufficient to raise its m. p. to 170–171°.

cohol. Two small crops of white, felty needles, m. p. 203-205° after recrystallization, were obtained. A mixed melting point with dibenzaldiaminoguanidine nitrate was the same. Further evaporation of the alcohol solution yielded no more crystalline material and left a reddish-brown oil from which a small amount of benzalazine was extracted by trituration with diethyl ether. Other attempts to purify the oil by crystallization failed. Further separation of the compounds in this oil was accomplished by precipitating solid picrates from alcoholic solution. Fractionation of these picrates gave two materials: (1) A compound which was only sparingly soluble in boiling 95% ethyl alcohol and which decomposed at 241–243° after one recrystallization; a mixed melting point with a sample of dibenzaldiaminoguanidine picrate was 241°. (2) A picrate which was readily soluble in hot ethanol and which decomposed at 161–162° after two recrystallizations; a mixed melting point with an authentic sample of benzal-1-*n*-butyl-3-aminoguanidine picrate was 166–167°.

Benzal 1-*n*-Butyl-3-aminoguanidine Picrate.—Twenty-one milliliters of glacial acetic acid was added dropwise during twenty minutes to a slurry of 8.0 g. of 1-*n*-butyl-3-nitroguanidine (0.05 mole), 13.0 g. of zinc dust, and 75 ml. of water. The mixture was vigorously stirred and the temperature maintained at 30–35°. The agitation was continued for twenty minutes longer before the colorless solution was filtered from a small quantity of unreacted zinc. The filtrate was acidified with 5 ml. of concentrated nitric acid (sp. gr. 1.4), warmed to 60°, and shaken with 5 ml. of benzaldehyde. A pink colored viscous oil separated after overnight cooling at 0°. The aqueous layer was decanted and discarded and the oil dissolved in 60 ml. of 95% ethyl alcohol. This latter solution was added to a boiling solution of 10 g. of picric acid in 100 ml. of 95% ethyl alcohol. The yield of solid picrate, m. p. 167–168.5°, crystallizing from the cooled solution was 11.4 g. (39.5%). Recrystallization from 95% ethanol did not change the melting point.

Anal. Calcd. for $C_{15}H_{21}O_7N_7$: C, 48.32; H, 4.73; N, 21.92. Found: C, 48.46, 48.36; H, 4.82, 4.73; N, 22.31, 22.38.

Reaction of Hydrazine Hydrate and 1-Methyl-3-nitroguanidine.—Ten grams of methylnitroguanidine[4] (0.085 mole), 5.0 g. of hydrazine hydrate (0.1 mole), and 50 ml. of water were heated at 65–70° for thirty minutes. Ammonia and nitrous oxide were evolved and the solution became deep orange in color. The solution was cooled, neutralized with 115 ml. of 1 *N* sulfuric acid, and diluted with 95% ethanol until a turbidity developed. Chilling this solution at 0 to 5° yielded 6.5 g. of orange-colored crystals, melting at 205°. The impure product was purified by redissolving in a 25 ml. of water, filtering, diluting the filtrate with 95% ethanol until a turbidity developed, and chilling at 0°. Three recrystallizations gave a white product melting sharply at 227–228°.

Anal. Calcd. for diaminoguanidine sulfate, $2CH_7N_5 \cdot H_2SO_4$: S, 11.60. Found: S, 11.72, 11.76.

The purified sulfate gave a picrate from water solution which melted at 188° after recrystallization from alcohol. A mixed melting point with a sample of diaminoguanidine picrate[8] was also 188°.

Summary

1. The principal products formed in the hydrazinolysis of nitroguanidine in aqueous solution are nitroaminoguanidine, aminoguanidine and diaminoguanidine.
2. The hydrazinolysis of nitroaminoguanidine gives diaminoguanidine.
3. The hydrazinolysis of 1-*n*-butyl-3-nitroguanidine in aqueous solution gives nitroaminoguanidine and diaminoguanidine. In ethyl alcohol 1-*n*-butyl-3-aminoguanidine and diaminoguanidine are formed.

(8) Pellizzari and Cantoni, *Ber.*, **38**, 293 (1905), reported a m. p. of 191°.

China Lake, California Received September 13, 1949

[Contribution No. 167 from the Goodyear Research Laboratories]

Crystallization in High Polymers. V. Dependence of Melting Temperatures of Polyesters and Polyamides on Composition and Molecular Weight[1,2]

By Robert D. Evans, Harold R. Mighton[3a] and Paul J. Flory[3b]

In the preceding paper[4] of this series a general treatment of the configurational statistics of semicrystalline polymers was developed on the assumption that the crystalline and amorphous regions, or zones, are separated by distinct boundaries such as those normally occurring between contiguous phases of heterogeneous substances. The theory leads to the concept of an equilibrium melting temperature T_m at which crystallinity disappears completely, this temperature being characteristic of a given polymer in the same way that the melting point of a crystalline compound is characteristic of the substance. Although melting may take place over a range of temperatures preceding T_m, final disappearance of crystallinity is predicted to occur at a definitive temperature above which finite amounts of crystallinity become thermodynamically unstable.

Of the various deductions which follow from the theory,[4] those pertaining to the dependence of T_m on composition are most provocative of experiment. Three such relationships have been derived, expressing, respectively, the dependence of T_m on copolymer composition, on polymer chain length and on degree of dilution with a low molecular weight diluent. Thus, the melting temperature of a random copolymer was predicted to depend on its composition in accordance with the relationship

$$1/T_m - 1/T_m^0 = -(R/h_u) \ln X_A \qquad (1)$$

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[1] The work presented in this paper comprises a part of a program of fundamental research on rubber and plastics carried out under contract between the Office of Naval Research and the Goodyear Tire and Rubber Company.

[2] Presented before the High Polymer Forum at the 112th Meeting of the American Chemical Society, New York, New York, September 16, 1947.

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[4] P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).