α-n-Butylaminoisovaleronitrile. To isobutyraldehyde cyanohydrin (198 g., 2 moles) was added *n*-butylamine (185 g., 2.5 moles) with cooling to maintain the temperature at 25–30°. The mixture was stirred at room temperature for 6 hr. Benzene (150 ml.) was added and the water layer was separated and discarded. The benzene layer was distilled through a 4-inch Vigreux column, to give 235 g. (77%), b.p. 85–90°/5 mm., n_D^{25} 1.4358.

Anal. Calcd. for $C_9H_{18}N_2$: N, 18.2; neutral equivalent (nonaqueous), 154. Found: N, 17.7; neutral equivalent, 154.

Reaction of α-n-butylaminoisovaleronitrile with hydroxylamine hydrochloride. To a suspension of hydroxylamine hydrochloride (29 g., 0.42 mole) in methanol (150 ml.) was added *α-n*-butylaminoisovaleronitrile (51 g., 0.33 mole) dropwise. A slight exotherm developed, the solution became clear, and HCN was evolved. After 2 hr., there was added a solution of Na_2CO_3 (22 g., 0.23 mole) in water (150 ml.). Further dilution failed to give the expected precipitate. The mixture was evaporated *in vacuo* to remove methanol, and an oil separated. From this oil, after storing overnight, fine needles precipitated, which were filtered off. The solid (7 g.) was crystallized from 1:1 benzene-hexane mixture to give 1.8 g., m.p. 85°, whose analysis was fairly close to that of the amidoxime (% N found, 23.0), but which was not identified as such.

Ethylene bis(iminodiacetamidoxime). To a slurry of ethylene bis(iminodiacetonitrile) (10.0 g., 0.047 mole) in methanol (25 ml.) was added a solution of hydroxylamine hydrochloride (14.0 g., 0.2 mole) in water (15 ml.). Heat was evolved. Stirring was continued for 1 hr., and then sodium carbonate (10.6 g., 0.1 mole) slowly added. After 3 hr. additional stirring, the mixture was filtered, and the residue dried in air. The crude product, 15.5 g. (95%), m.p. 182–184°, was purified by recrystallization from distilled water, m.p. 186–187° with decomposition.

Anal. Calcd. for $C_{10}H_{24}O_4N_{10}$: C, 34.5; H, 6.9; N, 40.2. Found: C, 34.4; H, 6.9; N, 40.3.

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PHILADELPHIA, PA.

[CONTRIBUTION FROM EASTERN LABORATORY OF EXPLOSIVES DEPARTMENT, E. I. DU PONT DE NEMOURS & CO., INC.]

Dinitro Amines and Their Reduction Products from the Mannich Reaction of Nitrocyclohexane with Aliphatic Diamines or Ammonia

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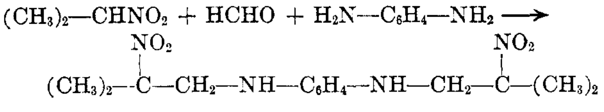
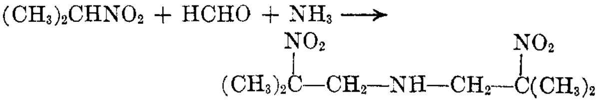
Nitrocyclohexane was found to react readily with aliphatic primary or secondary diamines or ammonia in the Mannich reaction to give a new series of dinitroamines in good yield. The dinitro compounds were reduced to the corresponding polyamines.

The use of diamines in the Mannich reaction of secondary nitro paraffins was first recorded by Johnson when he described a dinitro diamine obtained from the reaction of 2-nitropropane with formaldehyde and *p*-phenylenediamine.[1] The product, *N,N'*-bis(2-nitroisobutyl)-*p*-phenylenediamine, is the compound obtained when one hydrogen from each of the two amine groups of the diamine is replaced by a 2-nitroisobutyl group leaving the amine groups secondary. More recently, Butler recorded the reaction of 2-nitropropane with formaldehyde and the secondary diamines, piperazine and 2,5-dimethylpiperazine.[2] He also obtained dinitro diamines although the amine groups in these products were both tertiary.



$$(CH_3)_2\text{—}CHNO_2 + HCHO + H_2N\text{—}C_6H_4\text{—}NH_2 \longrightarrow (CH_3)_2\text{—}\overset{\overset{\displaystyle NO_2}{|}}{C}\text{—}CH_2\text{—}NH\text{—}C_6H_4\text{—}NH\text{—}CH_2\text{—}\overset{\overset{\displaystyle NO_2}{|}}{C}\text{—}(CH_3)_2$$

The possibility of using ammonia in place of an amine in this type of reaction of secondary nitro paraffins was investigated by Urbanski with 2-nitropropane.[3] The product he isolated was bis(2-nitroisobutyl)amine in which two of the ammonia hydrogens had been replaced by 2-nitroisobutyl group to produce a secondary amine.



$$(CH_3)_2CHNO_2 + HCHO + NH_3 \longrightarrow (CH_3)_2\overset{\overset{\displaystyle NO_2}{|}}{C}\text{—}CH_2\text{—}NH\text{—}CH_2\text{—}\overset{\overset{\displaystyle NO_2}{|}}{C}(CH_3)_2$$

The use of the secondary nitro compound, nitrocyclohexane, in the Mannich reaction does not appear to have been studied previously, since most work of this type has been limited to the more readily available 2-nitropropane. It has now been found, however, that nitrocyclohexane takes part quite readily in Mannich reactions and that good yields of dinitro diamines may be obtained from either primary or secondary aliphatic diamines or from ammonia. The secondary amines studied were limited to the closed ring diamines, piperazine and *C*-substituted piperazines, but since secondary monoamines such as diisobutylamine react readily,[4]

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[1] H. G. Johnson, *J. Am. Chem. Soc.*, **68**, 14 (1946).

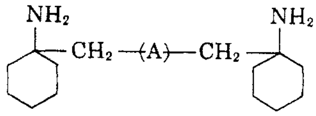
[2] G. B. Butler, *J. Am. Chem. Soc.*, **78**, 482 (1956).

[3] J. K. N. Jones and T. Urbanski, *J. Chem. Soc.*, 1766 (1949).

[4] R. A. Smiley, unpublished.

TABLE I

POLYAMINES



Basic Compound from Which Polyamine Is Derived (A)	% Yield	n_D^{25}	M.P. or B.P.	Analysis Calcd. / Found % C	% H	% N
Ammonia	77	1.5050	B.p. 134–135°	70.29	12.12	16.72
			(0.4 mm.)	70.54	11.60	17.58
Ethylenediamine	48	1.5067	B.p. 167–168°	68.08	12.05	19.85
			(0.55 mm.)	68.37	11.09	19.34
Hexamethylenediamine	47	1.4995	B.p. 194°	71.00	12.42	16.51
			(0.1 mm.)	71.01	12.47	16.35
Piperazine	65	—	M.p. 91–92°	70.10	11.69	18.19
				69.98	11.69	18.18
2-Methylpiperazine	73	1.5106	B.p. 174–179°	70.80	11.80	17.39
			(0.3 mm.)	70.11	11.53	17.35
trans-2,5-Dimethylpiperazine	75	—	M.p. 71–72°	71.85	11.97	16.16
				71.31	11.81	16.40

it seems probable that open-chain secondary diamines would react just as well as the piperazines.

All of the nitro amines prepared in this study were hydrogenated in ethanol with Raney nickel catalyst to the corresponding polyamines. Table I shows the properties of these compounds. These polyamines are all colorless and have no appreciable odor. When pure they appear to be quite stable and show no discoloration after normal storage for a year. They are all soluble in most organic compounds but are insoluble in water except for the ethylenediamine derivative. This compound is completely miscible in water and in all the organic liquids tested, including hydrocarbons.

EXPERIMENTAL

Materials. The nitrocyclohexane used in this study was prepared by the liquid-phase nitration of cyclohexane. The 2-methylpiperazine and the *cis*- and *trans*-2,5-dimethylpiperazine were obtained from the Wyandotte Chemical Corp. and were used without further purification. The formaldehyde was commercial formaldehyde solution meeting ACS specifications while all other reactants were of the best grade obtainable from commercial sources and were used as received.

Purification of nitrocyclohexane. Straw-colored, technical-grade nitrocyclohexane (500 ml.) was added dropwise to a stirred 500-ml. volume of concentrated sulfuric acid cooled in an ice bath. When the addition was complete, the solution was poured into a mixture of cyclohexane (500 ml.) and ice. The mixture was stirred until the ice melted. The cyclohexane layer was separated and dried over calcium chloride. The cyclohexane then was distilled off at atmospheric pressure, and the residue was distilled through a Claisen head *in vacuo.* Nitrocyclohexane purified in this manner was water white, boiled sharply at 79° at 10 mm., and had an n_D^{25} of 1.4587. Analysis of the distilled nitrocyclohexane by an infrared method failed to detect the presence (0.1%) of any alcohol, nitrate, or nitrite. The ketone content was usually about 0.2–0.6% by weight.

N,N'-Bis[(1-nitrocyclohexyl)methyl]piperazine. A solution of 64.5 g. (0.5 mole) of nitrocyclohexane, 50 g. (0.6 mole) of 37% formaldehyde, and 49 g. (0.25 mole) of piperazine hydrate in 250 ml. of 95% ethanol was stirred for 1 hr. at room temperature and then was refluxed on a steam bath for 2 hr. The thick white slurry which resulted was cooled, and the solid material was removed by filtration. Recrystallization from benzene gave 81 g. (87.5%) of white product, m.p. 186–188°.

Anal. Calcd. for $C_{18}H_{32}N_2O_4$: C, 58.65; H, 8.69; N, 15.21. Found: C, 58.87; H, 8.63; N, 15.49.

The following C-substituted piperazine derivatives were prepared in a similar manner.

N,N'-Bis[(1-nitrocyclohexyl)methyl]-2-methylpiperazine. M.p. 122–123°, yield 73%.

Anal. Calcd. for $C_{19}H_{34}N_4O_4$: C, 59.65; H, 8.90; N, 14.65. Found: C, 59.63; H, 8.57; N, 14.91.

N,N'-Bis[(1-nitrocyclohexyl)methyl]-2,5-dimethylpiperazine. The *trans*-diamine produced a white solid product in 76% yield, m.p. 149–150°, while the *cis*-diamine gave a 79% yield of product, m.p. 122–124°.

Anal. Calcd. for $C_{20}H_{36}N_4O_4$: C, 60.60; H, 9.09; N, 14.13. Found: C, 60.39; H, 9.02; N, 13.93.

N,N'-Bis[(1-nitrocyclohexyl)methyl]ethylenediamine. Ethylenediamine (15 g., 0.25 mole) was added slowly over a period of 30 min. to a stirred mixture of 64.5 g. (0.5 mole) of nitrocyclohexane and 50 g. (0.6 mole) of 37% aqueous solution of formaldehyde at a rate such that the temperature of the reaction mixture did not exceed 40°. After the addition of the diamine was complete, the reaction mixture was stirred for 4 hr. The mixture then was allowed to stand for 16 hr., after which time it was poured into 200 ml. of 18% hydrochloric acid. The white precipitate which formed was removed by filtration, washed with acetone, and dried. A yield of 71 g. (90%) of the dihydrochloride of the dinitro diamine was obtained.

The salt was neutralized with ammonium hydroxide, and the free dinitro diamine was removed by filtration. The product was recrystallized from diethyl ether, and a yield of 53 g. (75%) of white crystalline product, m.p. 72–73°, was obtained.

Anal. Calcd. for $C_{16}H_{30}N_4O_4$: C, 56.10; H, 8.77; N, 16.37. Found: C, 56.06; H, 8.77; N, 16.06.

N,N'-Bis[(1-nitrocyclohexyl)methyl]hexamethylenediamine. Using hexamethylenediamine in a manner similar to that used with ethylenediamine, a 32% yield of product was obtained which after recrystallization from a mixture of ethyl ether and 30–60° petroleum ether melted at 51–52°.

Anal. Calcd. for $C_{20}H_{38}N_4O_4$: C, 60.30; H, 9.55; N, 14.07; neut. equiv., 199.0. Found: C, 61.09; H, 9.40; N, 14.25; neut. equiv., 199.5.

Bis(1-nitrocyclohexylmethyl)amine. To a stirred solution of 258 g. (2 moles) of nitrocyclohexane and 270 g. (2.75 moles) of concd. ammonium hydroxide (28%) in 500 ml. of 95% ethanol was added 180 g. (2.2 moles) of 37% formaldehyde dropwise over a period of 1 hr. When the addition of formaldehyde was complete, the reaction mixture was refluxed for 4 hr. and then allowed to cool to room temperature. The mixture was poured into a liter of 1/1 solution of concentrated hydrochloric acid and water. The hydrochloride salt which precipitated was removed by filtration, washed in ethanol, and dried. The hydrochloride was neutralized with aqueous sodium hydroxide solution, and the free amine was recrystallized from 95% ethanol. The yield of white crystalline product, m.p. 57–58°, was 176 g. or 59%.

Anal. Calcd. for $C_{14}H_{24}N_3O_4 \cdot HCl$: C, 50.07; H, 7.74; N, 12.51. Found: C, 50.24; H, 7.66; N, 12.58.

The infrared spectra of all of the dinitro compounds showed a high nitro group absorption at 6.50–6.52, typical of tertiary nitro compounds.[5]

Reduction of dinitro amines to polyamines. All of the Mannich condensation products were reduced to the corresponding polyamines with hydrogen in a Parr hydrogenator by using 2 g. of Raney nickel[6] for 0.1 mole of dinitro compound in 175 ml. of 95% ethanol. The heavy-walled reaction bottle was shaken until the hydrogen required for the reduction of the nitro groups was absorbed. Then the catalyst was filtered off and the ethanol solvent removed under reduced pressure. The liquid products were purified by distillation *in vacuo*. The piperazine derivative was recrystallized from acetone, while the 2,5-dimethylpiperazine compound was recrystallized from 90–120° petroleum ether at −15°. Table I lists the properties of these compounds.

GIBBSTOWN, N. J.

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[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, PLASTICS DIVISION, MONSANTO CHEMICAL CO.]

Synthesis of Polyfunctional Polymers[1]

JOSEPH A. BLANCHETTE AND JOHN D. COTMAN, JR.

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Polyfunctional polymers were synthesized by chemical modification of hydrocarbon and nitrile polymers and by copolymerization of selected monomers. Reactions included aromatic nitration, chloromethylation and acylation, reduction of nitro, oximino, carbonyl and nitrile groups and other carbonyl reactions. Polymers utilized included polystyrene, polyacrylonitrile, and copolymers of methyl vinyl ketone with acrylonitrile and styrene.

Chemical modification of high polymers has been studied extensively. In this study polystyrene was chosen as a base polymer for modification because of the ready reactivity of the benzene ring to well defined products of definite structure for a number of reactions. Nitropolystyrene was prepared as a precursor of a variety of substituted polystyrenes such as aminopolystyrene and the products of reaction of diazotized aminopolystyrene. The nitrated polymer has been previously prepared[2–5] under conditions resulting in varying degrees of polymer degradation because of the vigor of the nitrating techniques (use of concentrated sulfuric and nitric acid mixtures at elevated temperatures). Acetylnitrate is an efficient nitrating agent at moderate temperatures, however, and should effect nitration of polystyrene without simultaneous polymer degradation. To increase the solubility of polystyrene in nitrating media, several polystyrenes of low molecular weight were prepared by polymerization in the presence of bromotrichloromethane (1–6%) as a chain transfer agent (Table I).

Nitropolystyrene was obtained when acetylnitrate was used as the nitrating agent and elemental analysis showed this material to contain less than one nitro group per benzene ring (0.6). Varying the conditions of reaction with acetyl nitrate did not yield a $—NO_2$ to C_6H_5 ratio greater than .6 (Table II).

Concentrated nitric acid did not dissolve polystyrene and, as would be expected, nitration was negligible. Fuming nitric acid reacted with polystyrene at 0° to yield a viscous sirup and considerable nitration occurred. Elemental analysis on the product corresponded to 1.2 nitro groups per benzene ring. Chemical and catalytic hydrogenations were carried out on the low molecular weight nitropolystyrenes. Chemical reduction was ineffectual. Products from catalytic hydrogenation (palladium-on-carbon catalyst) appeared to be aminopolystyrene[7–9] with infrared bands at 1600

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(1) This paper was presented at the November 1957 Meeting in Miniature of the Connecticut Valley Section of the American Chemical Society, Hartford, Conn.

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