(dioxan). An ethanol solution exhibited maxima at 270 and 362 mμ immediately after preparation but after a few minutes the peaks were at 270 and 323 mμ and both increased in intensity with time.

Anal. Calcd. for $C_{28}H_{29}N_2O_3$: C, 76.35; H, 6.39; N, 6.36. Found: C, 76.73; H, 6.20; N, 6.06.

1-Benzyl-3-acetylpyridinium chloride from the dimolecular pseudo base ether. Hydrogen chloride was passed into a solution of the dimolecular pseudo base ether (229 mg., 0.52 mmole) in 20 ml. of methanol for one minute. Evaporation of the solvent left a brown solid (235 mg., 91%) the infrared spectrum of which was identical with that of 1-benzyl-3-acetylpyridinium chloride. Recrystallization from methanol–ethyl acetate gave a 64% recovery of tan crystals which melted at 183.5–184° alone and when mixed with an authentic sample.

1-Benzyl-3-acetyl-4-cyano-1,4-dihydropyridine (VII). A solution of 3.25 g. (0.05 mole) of potassium cyanide in 10 ml. of water was added to a solution of 1.24 g. (0.005 mole) of 1-benzyl-3-acetylpyridinium chloride in 10 ml. of water. There was an immediate separation of a yellow oil. The supernatant solution was decanted from the oil and the latter washed with water and taken up in 5 ml. of hot ethanol. The yellow needles (0.87 g., 77%) which separated from the cooled solution melted at 114–115.5° with decomposition. An ethanol solution showed absorption at 351 mμ (ϵ 9,500).

Anal. Calcd. for $C_{15}H_{14}N_2O$: C, 75.60; H, 5.92. Found: C, 75.61; H, 5.99.

1-Benzylpyridinium-3-carboxylate (IX). 1-Benzyl-3-carbamoylpyridinium chloride (2.49 g., 0.01 mole) was dissolved in 100 ml. of 0.1*N* carbonate-free sodium hydroxide. The odor of ammonia was soon evident. After 2 hr. the solution was extracted with three 50-ml. portions of chloroform and then seven 50-ml. portions of 1-butanol. The combined butanol extracts were washed with 25 ml. of water, dried over sodium sulfate, and concentrated to a volume of 20 ml. Addition of a large excess of ether precipitated an orange solid (1.29 g., 60%). Purification by extraction with cold chloroform, chromatography on acid-washed alumina with methanol, treatment with Norit, and recrystallization from ethanol–ethyl acetate gave 0.8 g. (37.5%) of IX as colorless crystals, m.p. 183–184.5° dec.; λ_{max} (ethanol) 264 mμ. Treatment of this product with hydrochloric acid gave 1-benzyl-3-carboxypyridinium chloride, identical with a sample prepared from benzyl chloride and nicotinic acid. Acidification of the aqueous layer from the 1-butanol extraction with hydrochloric acid, extraction with chloroform and then 1-butanol (two 60-ml. portions), and evaporation of the butanol solution afforded 227 mg. of somewhat impure 1-benzyl-3-carboxypyridinium chloride.

SEATTLE 5, WASH.

[CONTRIBUTION FROM THE ROHM & HAAS CO.]

Nitrile Groups. V. Substituted Aminoacetamidoximes[1]

CHARLES S. HOLLANDER, ROBERT A. YONCOSKIE, AND PETER L. DE BENNEVILLE

Received February 26, 1958

The reaction of substituted aminoacetonitriles with hydroxylamine hydrochloride gave, after neutralization, substituted aminoacetamidoximes. The reaction is interpreted to reflect activation of the nitrile group by the ammonium ion. *N*-Benzyl-*N*-cyanomethyl-*N*,*N*-dimethylammonium chloride similarly gave a quaternary ammonium substituted acetamidoxime by reaction with free hydroxylamine. Aminonitriles derived from isobutyraldehyde and from cyclohexanone failed to give the reaction, and instead amine displacement reactions occurred. Tetrakis(cyanomethyl)ethylenediamine gave the corresponding tetrakisamidoxime.

Other papers in this series have shown that a nitrile group in a position near to an electron-withdrawing substituent undergoes reaction with amines with unusual ease.[1,2] The reactions to be described illustrate how a proximate cation (substituted ammonium group) favors the addition of hydroxylamine to the nitrile function.

The usual conditions for the formation of amidoximes require treating the corresponding nitrile with free hydroxylamine in aqueous alcoholic solution for an extended period of time. It is significant that unusually rapid reactions have been reported for succinonitrile,[3] cyanogen,[4] and tribromoacetonitrile.[5]

When, in this study, hydroxylamine was added to substituted aminoacetonitriles, it was not necessary, and not desirable, to free the hydroxylamine from its hydrochloride by the addition of a base. The reaction of the nitrile with hydroxylamine hydrochloride proceeded rapidly with evolution of heat to give the hydrochloride of the corresponding aminoacetamidoxime. The addition of sodium carbonate in equivalent amount then freed the amidoxime for isolation. The data for a number of aminoacetamidoximes are given in Table I.

The aminonitrile is believed to take part in the reaction in its ammonium form, by equilibration with the hydroxylamine hydrochloride. The provision in this way of a highly electron-withdrawing substituent then activates the nitrile group. This substituent could also be provided in the form of a quaternary ammonium ion, in which case it would be necessary to add base to free the hydroxylamine for reaction. *N*-Benzyl-*N*,*N*-dimethyl-*N*-cyanomethylammonium chloride was prepared, and to it was added an equivalent amount of hydroxylamine

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(1) For the previous paper in this series, see P. L. de Benneville, C. L. Levesque, L. J. Exner, and E. Hertz, *J. Org. Chem.*, **21**, 1072 (1956).

(2) (a) L. J. Exner, M. J. Hurwitz, and P. L. de Benneville, *J. Am. Chem. Soc.*, **77**, 1103 (1955); (b) M. J. Hurwitz, L. J. Exner, and P. L. de Benneville, *J. Am. Chem. Soc.*, **77**, 3251 (1955).

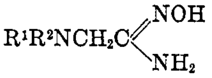
(3) F. Sembritzki, *Ber.*, **22**, 2958 (1899).

(4) E. Fischer, *Ber.*, **22**, 1930 (1899).

(5) W. Steinkopf and H. Grünupp, *Ber.*, **41**, 3571 (1908).

TABLE I

SUBSTITUTED AMINOACETAMIDOXIMES

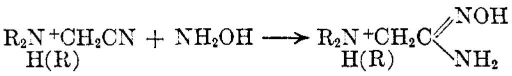


$$R^1R^2NCH_2C\begin{matrix}\nearrow NOH\\ \searrow NH_2\end{matrix}$$

R¹	R²	M.P., °C.	Yield, %	Empirical Formula	% C Calcd.	% C Found	% H Calcd.	% H Found	% N Calcd.	% N Found
CH_3	CH_3	112–114	22	$C_4H_{11}N_3O$	41.0	41.5	9.4	9.7	35.9	35.9
C_2H_5	C_2H_5	79–80[a]	51	$C_6H_{15}N_3O$	49.6	49.6	10.3	10.4	29.0	29.2
Morpholine		152–153[b]	52	$C_6H_{13}N_3O_2$	45.3	45.4	8.2	8.1	26.4	26.4
n-C_4H_9	H	84–85[c]	64	$C_6H_{15}N_3O$	49.6	49.4	10.3	10.4	29.0	28.7
t-C_8H_{17}[d]	H	95–96	72	$C_{10}H_{23}N_3O$	59.7	59.5	11.4	11.6	20.9	20.6
C_6H_{11}[e]	H	146–148[a]	71	$C_8H_{17}N_3O$	56.1	56.3	9.9	9.8	24.5	24.3

[a] Recrystallized from water. [b] Recrystallized from isopropyl alcohol. [c] Recrystallized from ethyl acetate. [d] t-C_8H_{17} is 1,1,3,3-tetramethylbutyl. [e] C_6H_{11} is cyclohexyl.

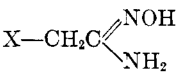
hydrochloride. No reaction took place. An equivalent amount of sodium carbonate solution was then slowly added, and before the addition was half over, heat was evolved, and the corresponding amidoxime was ultimately isolated. The general reaction is therefore probably best formulated:



$$\underset{H(R)}{R_2N^+}CH_2CN + NH_2OH \longrightarrow \underset{H(R)}{R_2N^+}CH_2C\begin{matrix}\nearrow NOH\\ \searrow NH_2\end{matrix}$$

Infrared spectra were obtained on a Perkin-Elmer Spectrophotometer, Model 21. Common peaks in the spectra determined in KBr dispersion (*ca.* 5% of the compound) for *N*-*n*-butyl- and *N*,*N*-dimethylaminoacetamidoxime, for acetamidoxime[6] itself, and for *N*-benzyl-*N*,*N*-dimethylammonium acetamidoxime chloride are given in Table II. The same peaks (except where Nujol interferes) were present in Nujol mulls of these compounds, and of *N*-(1,1,3,3-tetramethylbutyl)- and *N*-cyclohexylaminoacetamidoxime.

TABLE II



INFRARED PEAKS (CM.$^{-1}$) COMMON TO $X—CH_2C\begin{matrix}\nearrow NOH\\ \searrow NH_2\end{matrix}$

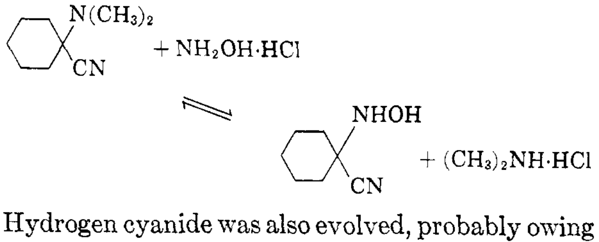
X = n-C_4H_9NH	$(CH_3)_2N$	$C_6H_5CH_2\overset{+}{N}(CH_3)_2$	H
3436	3401	3396	3484
3247	3247	3300	3356
3086	3106 (b)	3115	3106 (b)
2882	2907 (s)	2905 (s)	2924 (s)
2778 (b)	2778 (b)	2778 (m)	2762
1661	1664	1661	1661
1610 (m)	1618	1603 (m)	1590
1499 (w)	1499 (m)	1479 (m)	Absent
1451 (m)	1451	1449 (m)	1414 (m)
1387 (m)	1404	1389 (m)	1399
1340 (w)	1340 (m)	1355 (w) 1342 (w)	1366
995 (w)	992	999 (w)	Absent

(b) = broad; (s) = shoulder; (m) = medium; (w) = weak

Strong absorption was present in the whole range from 3450 to 2780 cm.$^{-1}$ Medium, fairly sharp peaks were obtained for the quaternary salt and for unsubstituted acetamidoxime at 2778 and 2762 cm.$^{-1}$, and a sharp drop in absorption followed to the base line at about 2600 cm.$^{-1}$ On the other hand, the two amino compounds gave strong, broad bands at 2778 cm.$^{-1}$, and a slow regular drop in absorption followed to the base line at about 2300 cm.$^{-1}$ These absorption characteristics are interpreted as reflecting inter- and intramolecular bonding.[7]

Absorptions at 1661–1664 cm.$^{-1}$ for C═N, and at 1590–1618 cm.$^{-1}$ for NH_2 were at the expected locations for these functional groups. Bonded NH and OH gave three peaks at slightly different locations for all four compounds in the 3100–3500 region.

α-Aminonitriles derived from isobutyraldehyde and from cyclohexanone did not give the same reaction. Instead, amine displacement reactions occurred.[8] When 1-dimethylaminocyclohexanecarbonitrile was heated in aqueous alcohol with hydroxylamine hydrochloride, 1-hydroxaminocyclohexanecarbonitrile was produced in significant amounts:



Hydrogen cyanide was also evolved, probably owing to reversion of the aminonitriles in the presence of

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(6) Prepared by the method of E. Nordmann, *Ber.*, **17,** 2746 (1884).

(7) The 2778 cm.$^{-1}$ peak is the most characteristic element of these spectra, but its assignment is quite conjectural. The broader absorption from 2800 to 2300 cm.$^{-1}$ in the amino compounds may be caused by intra- and intermolecular bonding involving the free electron pair on the amino-nitrogen atom and the amidoxime group. The quaternary salt with no free electrons resembles the unsubstituted amidoxime in lacking this.

(8) The particular carbonyl derivatives were chosen for ease of isolation. The results, which can probably be generalized for ketones and aldehydes other than formaldehyde, indicate that the activation of the nitrile group may involve removal of a proton from the central active methylene group as the first step of the reaction.

water; in another experiment, carried out over a long period of time, cyclohexanone oxime was the major product isolated. The reaction of α-*n*-butylaminoisovaleronitrile with hydroxylamine hydrochloride also evolved hydrogen cyanide, and there was isolated only a small amount of an impure crystalline solid.

The reaction can be carried out with more than one cyanomethyl group on the nitrogen atom. Thus, *N,N,N',N'*-tetrakis(cyanomethyl)ethylenediamine was converted to the tetrakis-amidoxime in good yield by the same procedure.

EXPERIMENTAL

Starting materials. Dimethylaminoacetonitrile,[9] cyclohexylaminoacetonitrile,[10] and 1,1,3,3-tetramethylbutylaminoacetonitrile[11] were prepared from commercial 50–70% aqueous glycolonitrile and isolated as pure compounds. Diethylaminoacetonitrile, *N*-cyanomethylmorpholine, and *n*-butylaminoacetonitrile were prepared from the corresponding amines and aqueous glycolonitrile, and were used as the resulting aqueous solutions, as described herein. *N,N,N',N'*-Tetrakis(cyanomethyl) ethylenediamine[12] was prepared from ethylenediamine, formaldehyde, and hydrogen cyanide.

Substituted aminoacetamidoximes. The following procedures illustrate several isolation procedures, which depend on the water solubility of the product, as well as the use of a substituted aminoacetonitrile prepared and used in aqueous solution.

Dimethylaminoacetamidoxime. To a solution of dimethylaminoacetonitrile (42 g., 0.5 mole) in ethanol (100 ml.) was added over a period of 10 min. at room temperature a solution of hydroxylamine hydrochloride (35 g., 0.5 mole) in water (35 ml.). A slight exotherm resulted which was allowed to dissipate. To the solution was then added solid sodium carbonate (26.5 g., 0.25 mole) in portions, and the mixture was stirred for 1 hr. The precipitated NaCl was removed by filtration and the filtrate evaporated to a moist solid. This was recrystallized from isopropyl alcohol to give 13 g. (22%), m.p. 107–112°, which was purified without loss by another recrystallization. The product was water-soluble.

1,1,3,3-Tetramethylbutylaminoacetamidoxime. To a solution of 1,1,3,3-tetramethylbutylaminoacetonitrile (83 g., 0.5 mole) in ethanol (150 ml.) was added a solution of hydroxylamine hydrochloride (35 g., 0.5 mole) in water (150 ml.), with ice water cooling. The mixture was stirred for 30 min. after which cooling was removed. After about 1 hr., the solution was clear, and a slight exotherm was still apparent. When no more heat was evolved, there was added a solution of sodium carbonate (26.5 g., 0.25 mole) in water (100 ml.). The ethanol was removed *in vacuo,* and the reaction mixture was filtered. The precipitate, m.p. 92–94°, amounted to 56.5 g., and a second crop of 16 g., m.p. 72–77°, was obtained by further evaporation. Both crops, when recrystallized from 1:1 methanol-water mixtures, melted at 92–94°. The total, based on isolated crude, was 72.5 g. (72%).

Diethylaminoacetamidoxime. To a 70% aqueous glycolonitrile solution (27 g., 0.33 mole) was added diethylamine (24.3 g., 0.33 mole) with good cooling. After standing overnight, the water layer was separated, and the crude aminonitrile (39 g.) was diluted with methanol (100 ml.). The solution was added gradually with stirring to a solution of hydroxylamine hydrochloride (23.3 g., 0.33 mole) in water (75 ml.). Heat was evolved. The mixture was allowed to stand overnight, and to it was added a solution of sodium carbonate (17.7 g., 0.167 mole) in water. The solution was evaporated *in vacuo* at room temperature until crystals appeared. It was then cooled in ice water, and filtered to give 24.7 g. (51%) melting at 79–80° after recrystallization from water.

N-Benzyl-N,N-dimethylammoniumacetamidoxime chloride. A solution of dimethylaminoacetonitrile (21 g., 0.25 mole) and benzyl chloride (31.7 g., 0.25 mole) in isopropyl alcohol (50 ml.) was heated at reflux for 3 hr., at the end of which time all of the chlorine was ionizable, by Volhard titration. The solution was diluted with ethanol (100 ml.) and to it was added a solution of hydroxylamine hydrochloride (17.5 g., 0.25 mole) in water (50 ml.). No heat was evolved. A solution of sodium carbonate (13.3 g., 0.125 mole) in water (50 ml.) was slowly added, and heat was evolved when addition was about one-half over. The remainder of the carbonate solution was added and the mixture stirred for 2 hr. The water and ethanol were removed at room temperature *in vacuo* leaving a mixture of solid and oil which solidified overnight. To it was added anhydrous ethyl acetate (300 ml.), and the solid was thoroughly triturated, and filtered off. It was dried, taken up in methanol (200 ml.), and filtered to remove sodium chloride. The filtrate was refrigerated overnight. The crystals which formed were filtered to give 41.5 g. (59%) of the desired quaternary salt, which contained 12.6% ionizable chlorine and corresponded in analysis to a dihydrate. After drying in an Abderhalden pistol, the anhydrous crystals melted at 176–178° with decomposition.

Anal. Calcd. for $C_{11}H_{18}N_3OCl$: C, 54.2; H, 7.4; N, 17.2; Cl, 14.6. Found: C, 54.0; H, 7.5; N, 17.0; Cl (ionizable) 14.3.

1-Dimethylaminocyclohexanecarbonitrile. To an aqueous solution of dimethylamine (225 g. of 40% or 2 moles) was added cyclohexanone (172 g., 1.75 moles) dropwise at 10–15°. There was then added, with cooling, liquid hydrogen cyanide (54 g., 2 moles). The mixture was stirred for 1 hr. The organic layer was distilled through a 4-inch Vigreux column to give 217 g. (82%) of product, b.p. 79–83°/3 mm.

Anal. Calcd. for $C_9H_{16}N_2$: N, 18.4. Found: N, 18.0.

Reaction of 1-dimethylaminocyclohexanecarbonitrile with hydroxylamine hydrochloride. To a solution of the carbonitrile (51 g., 0.33 mole) in ethanol (100 ml.) was added a solution of hydroxylamine hydrochloride (25 g., 0.36 mole) in water (100 ml.). No heat was evolved. The mixture was stirred for 30 min., then heated at reflux for 20 min. HCN was evolved. The mixture was cooled, and to it was added a solution of sodium carbonate (19 g., 0.18 mole) in water (100 ml.). The ethanol was stripped *in vacuo,* the reaction mixture was cooled to 0°, and filtered. The crystalline product, 30.5 g., m.p. 73–80°, was combined with 2 g. obtained by further concentration, and the whole was recrystallized from isopropyl alcohol (HCN evolved) to give 8.5 g. of colorless solid, m.p. 133–135°. Further recrystallization of this from 80:20 isopropyl alcohol–water mixture improved the melting point to 137.5–138°. This material analyzed correctly for 1-hydroxaminocyclohexanecarbonitrile. Infrared spectrum (Nujol mull): Bonded NH and OH at 3240 (broad); $-C\equiv N$ at 2235 (weak); no absorption in 1500–1700 region.

Anal. Calcd. for $C_7H_{12}N_2O$: C, 60.0; H, 8.6; N, 20.0. Found: C, 59.9; H, 8.6; N, 20.0.

In another experiment of approximately 20 hr. duration, there was obtained from one mole of the carbonitrile, 104.5 g. of colorless solid, m.p. 87–89°, which was identified as cyclohexanone oxime, m.p. 89–90°.[13]

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(9) D. B. Luten, Jr., *J. Org. Chem.,* **3,** 588 (1938).

(10) L. J. Exner, L. S. Luskin, and P. L. de Benneville, *J. Am. Chem. Soc.,* **75,** 4841 (1953).

(11) L. S. Luskin, M. J. Culver, G. E. Gantert, W. E. Craig, and R. S. Cook, *J. Am. Chem. Soc.,* **78,** 4042 (1956).

(12) I. G. Farbenindustrie, A. G. French Patent **831,985;** *Chem. Abstr.,* **33,** 2913 (1939).

(13) A. Baeyer, *Ann.,* **278,** 102 (1894).

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., $n_{\rm D}^{25}$ 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.

Acknowledgments. The authors are grateful to Mr. Clyde Nash for analytical results, to Miss Helen Miklas and Mr. Hugo Ciccotosto for infrared spectra, and to Miss Rita Cerruti for several preparations of starting aminonitriles.

PHILADELPHIA, PA.

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

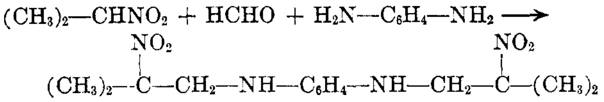
Dinitro Amines and Their Reduction Products from the Mannich Reaction of Nitrocyclohexane with Aliphatic Diamines or Ammonia

ROBERT A. SMILEY

Received December 5, 1957

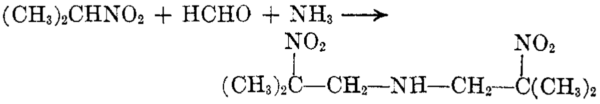
Nitrocyclohexane was found to react readily with aliphatic primary or secondary diamines or ammonia in the Mannich reaction to give a new series of dinitroamines in good yield. The dinitro compounds were reduced to the corresponding polyamines.

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.



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

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.



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

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.