filtered and the filtrate was distilled at 3 mm. Yield of 2-nitro-2-methyl-1,3-diisopropylaminopropane, b. p. 98–100° at 3 mm., was 161 g.; conversion, 71%.

Method B. From 2-Nitro-2-methyl-1,3-propanediol and Isopropylamine.—A solution of one mole of 2-nitro-2-methyl-1,3-propanediol (135 g.) and two moles of isopropylamine (118 g.) was allowed to stand in the room for three days. Distillation of the top layer gave 137 g. of nitro diamine; conversion, 60%.

III. Hydrogenation of Nitroamines to Polyamines

The nitro amines which were prepared were hydrogenated to the corresponding polyamines. The hydrogenation of each nitroamine and the isolation of the products were carried out as follows:

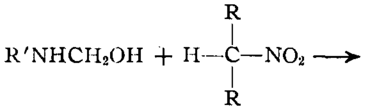
One hundred grams of nitroamine (either pure nitroamine or crude nitroamine which had not been rectified) was dissolved in 100 ml. of methanol and the solution was hydrogenated at 30–50° and 500 lb./sq. in. in the presence of 5 g. of Raney nickel. The solution was filtered and the filtrate was distilled at atmospheric pressure to remove the methanol. To the residue was added 200 ml. of benzene. A Dean and Stark moisture trap[6] which was connected to a condenser was fitted to the top of the column and the mixture was refluxed until water had ceased separating in the trap. Distillation of the residue was then resumed.

The conversion to pure polyamines, basis nitroparaffins, was the same whether the pure nitro amines or the crude nitro amines were hydrogenated.

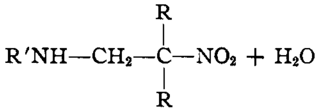
Lists of nitroamines and polyamines prepared together with some of their properties are given in Tables I and II.

Summary

It has been found that N-hydroxymethylalkylamines derivable from primary alkyl amines and formaldehyde will react with secondary nitroparaffins according to the following scheme

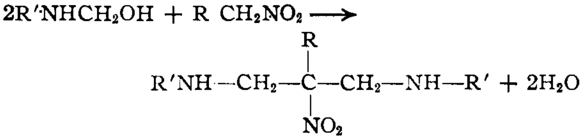


$$R'NHCH_2OH + H-\underset{R}{\overset{R}{C}}-NO_2 \longrightarrow$$



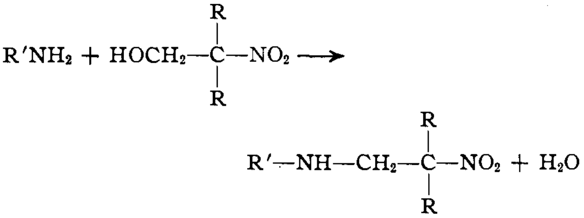
$$R'NH-CH_2-\underset{R}{\overset{R}{C}}-NO_2 + H_2O$$

It was shown that N-hydroxymethylalkylamines will react with primary nitroparaffins to give nitro diamines

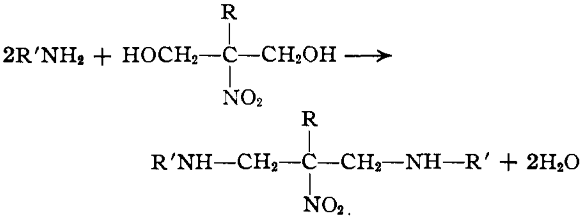


$$2R'NHCH_2OH + R\ CH_2NO_2 \longrightarrow R'NH-CH_2-\underset{NO_2}{\overset{R}{C}}-CH_2-NH-R' + 2H_2O$$

The above nitro compounds were also prepared by allowing the primary alkylamines to react with nitro alcohols derivable from the same nitroparaffins and formaldehyde according to the following schemes



$$R'NH_2 + HOCH_2-\underset{R}{\overset{R}{C}}-NO_2 \longrightarrow R'-NH-CH_2-\underset{R}{\overset{R}{C}}-NO_2 + H_2O$$



$$2R'NH_2 + HOCH_2-\underset{NO_2}{\overset{R}{C}}-CH_2OH \longrightarrow R'NH-CH_2-\underset{NO_2}{\overset{R}{C}}-CH_2-NH-R' + 2H_2O$$

The nitroamines that were prepared were hydrogenated to the corresponding polyamines.

TERRE HAUTE, INDIANA RECEIVED AUGUST 22, 1945

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(6) Dean and Stark, *Ind. Eng. Chem.*, **12**, 486 (1920).

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, COMMERCIAL SOLVENTS CORPORATION, TERRE HAUTE, INDIANA]

Reaction of Aliphatic Amines with Formaldehyde and Nitroparaffins. II. Secondary Amines*

BY HAL G. JOHNSON[1]

Essentially the results of the work described in this paper are an extension of the work of Senkus and also Henry, Mousset and Cerf as described in the preceding article.[1] The secondary nitroparaffins have been treated with formaldehyde and various aliphatic secondary amines. However, some primary nitroparaffin reactions with formaldehyde and secondary aliphatic amines also have been covered. The reaction was carried out by two different methods: A, reaction of the amines, formaldehyde and nitroparaffin; and B, reaction of the amine with the nitro alcohol or nitro diol. Although the same end-products result in either case, it is believed that the nitro alcohol or the nitro diol first decomposes into the nitroparaffin and formaldehyde. The relative rates of reaction are considered an indication of the mechanism.

The nitro amines which were prepared were all hydrogenated to the corresponding polyamines. These reduction products are also described here.

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* Prepared for the 1945 Meeting-in-Print of the Division of Organic Chemistry, ACS. For part I see Senkus, THIS JOURNAL, **68**, 10 (1946).

(1) Presently associated with the Dykern Company, St. Louis, Missouri.

TABLE I

NITRO AMINES

Starting materials Formaldehyde, 2-nitropropane and amine	Product	Conversion	Method of prepn.	Boiling point, °C.	Mm.	n^{20}_D	d^{20}_{20}	Formula	N[f] Content % Calcd.	Found
Dimethylamine	N-(2-Nitroisobutyl)-dimethylamine	74	A	65–66	10	1.4330	0.9784	$C_6H_{14}N_2O_2$	19.18	19.05
		73	B							
Dimethylamine[c]	N-(2-Nitro-2-methylbutyl)-dimethylamine	76	B	64	3	1.4410	0.9772	$C_7H_{16}N_2O_2$	17.71	17.71
Dibutylamine	N-(2-Nitroisobutyl)-dibutylamine	64	A	135	10	1.4453	0.9180	$C_{12}H_{26}N_2O_2$	12.12	12.38
		63	B							
Bis-(2-ethylhexyl)-amine	N,N-Bis(2-ethylhexyl)-2-nitroisobutylamine[b]							$C_{20}H_{42}N_2O_2$		
Piperidine	N-(2-Nitroisobutyl)-piperidine	83	B	82–83	0.5	20.1°C.[a]	1.0028	$C_9H_{18}N_2O_2$	15.05	15.09
2,5-Dimethylpyrrolidine	N-(2-Nitroisobutyl)-2,5-dimethylpyrrolidine	46	B	70–73	0.5	1.4622	0.9946	$C_{10}H_{20}N_2O_2$	13.99	14.12
Morpholine	N-(2-Nitroisobutyl)-morpholine	24	B	90–91	0.5	43.0°C.[a]		$C_8H_{16}N_2O_3$	14.89	14.78
Diethanolamine	3-(2-Nitroisobutyl)-3-aza-1,5-pentanediol[b]		B					$C_8H_{18}N_2O_4$		
Dimethylamine[d]	4-Nitro-2,4,6-trimethyl-2,6-diazaheptane	71	B			32.0[a]		$C_8H_{19}N_3O_2$	22.21	21.95
Dibutylamine[e]	2-Nitro-1,3-bisdibutylamino-2-methylpropane[b]		B					$C_{20}H_{43}N_3O_2$		

[a] Melting point. [b] High boiling material, purification not attempted. Crude material reduced to polyamine. [c] With 2-nitrobutane. [d] With nitroethane. [e] With nitroethane. [f] Dumas nitrogen.

TABLE II

POLYAMINES

Polyamine	Boiling point, °C.	Mm.	n^{20}_D	d^{20}_{20}	Formula	N[a] Content Calcd.	Found	Conversion, %[b]
N-(2-Aminoisobutyl)-dimethylamine	119	755	1.4216	0.7882	$C_6H_{16}N_2$	24.12	23.83	66a 48b
N-(2-Amino-2-methylbutyl)-dimethylamine	146	758	1.4318	.8076	$C_7H_{18}N_2$	21.85	21.57	86a
N-(2-Aminoisobutyl)-dibutylamine	89–90	6	1.4412	.8164	$C_{12}H_{28}N_2$	13.99	13.99	60a 37b
N,N-Bis-(2-ethylhexyl)-2-aminoisobutylamine	141–143	2	1.4547	.8346	$C_{20}H_{47}N_2$	8.97	8.90	70b
N-(2-Aminoisobutyl)-piperidine	60.5	6	1.4585	.8672	$C_9H_{20}N_2$	17.92	17.86	95a
N-(2-Aminoisobutyl)-2,5-dimethylpyrrolidine	59–60	3	1.4555	.8623	$C_{10}H_{22}N_2$	16.45	16.42	69a
N-(2-Aminoisobutyl)-morpholine	68	6	1.4595	.9402	$C_8H_{18}N_2O$	17.70	17.69	59b
3-(2-Aminoisobutyl)-2-aza-1,5-pentanediol	140	1	1.4888	1.0338	$C_8H_{20}N_2O_2$	15.90	15.86	25b
5-Amino-2,4,6-trimethyl-2,6-diazaheptane	36	40	1.4220	0.7989	$C_8H_{21}N_3$	26.40	25.97	30b
2-Amino-1,3-bis-dibutylamino-2-methylpropane	61–68	1			$C_{20}H_{45}N_3$	12.84	12.90	23b

[a] Kjeldahl nitrogen determinations. [b] a and b represent the two methods of preparation discussed in text.

Experimental

I. Preparation of Nitro Amines from Secondary Nitroparaffins and Secondary Alkyl Amines

Two methods were used for preparation of nitro amines from secondary nitroparaffins. These methods are described below in the preparation of N-(2-nitroisobutyl)-dimethylamine and N-(2-nitroisobutyl)-dibutylamine.

Method A. Preparation of N-(2-Nitroisobutyl)-dimethylamine from Dimethylamine, Formaldehyde and 2-Nitropropane.—In a two-liter, three-necked flask fitted with a condenser, a sealed stirrer, a thermometer reaching into the flask liquid and a dropping funnel was placed 351 g. (2 moles) of a 25.7% solution of dimethylamine. The flask was cooled by means of running water (18°) so that the temperature of the reaction mixture did not exceed 25° during the addition of two moles (166.7 g. of 35.8% solution) of formaldehyde through the dropping funnel. The mixture was stirred for an additional hour before 178 g. (2 moles) of 2-nitropropane was added all at once through the dropping funnel. The mixture was allowed to come to room temperature with continued stirring. Thirty grams of sodium chloride was added to salt out the non-aqueous layer which was separated and dried over anhydrous sodium sulfate. Distillation of the product through a five-foot column, packed with glass helices, gave 4 g. of material, b. p. up to 65° at 10 mm., and 212 g. of N-(2-nitroisobutyl)-dimethylamine, b. p. 65–66° at 10 mm. There was an additional 4 g. of material, b. p. 66–70° at 10 mm. and a residue of 7 g. The conversion to nitro amine was 72.5%.

Method B. Preparation of N-(2-Nitroisobutyl)-dibutylamine from 2-Nitro-2-methyl-1-propanol and Dibutylamine.—In a 500-ml. glass-stoppered bottle were placed 112.7 g. of 2-nitro-2-methyl-1-propanol (0.95 mole) and 122.2 g. of dibutylamine (0.95 mole). The mixture was shaken to dissolve the nitro alcohol and make the solution homogeneous. The mixture was left to stand at room temperature. After one day the solution became cloudy and water began to collect on the bottom of the bottle. Water continued to separate for four days at which time 13 ml. (theoretical 17.1 ml.) had separated. The bottle was then placed in a 50° water-bath for two days. Total water separated was 15.6 ml. The product, dried over anhydrous sodium sulfate, was distilled under vacuum in a five-foot column packed with glass helices to yield 44 g. of material, b. p. 45–113° at 8–10 mm., and 199 g. of N-(2-nitroisobutyl)-dibutylamine, b. p. 113–120° at 7–8 mm. (135° at 10 mm.). The residue (47 g.) was not distilled; conversion to nitro amine, 63%.

II. Preparation of Nitro Diamines from Secondary Alkyl Amines and Primary Nitroparaffins

While both methods described in Part I should be applicable here as they are for primary alkyl amines, actually only method B was used in preparing the compounds. It is illustrated below in the preparation of 4-nitro-2,4,6-trimethyl-2,6-diazaheptane.

Method B. Preparation of 4-Nitro-2,4,6-trimethyl-2,6-diazaheptane from 2-Nitro-2-methyl-1,3-propanediol and Dimethylamine.—A mixture of 351 g. of a 25.7% dimethylamine solution (2 moles) and 135 g. of 2-nitro-2-methyl-1,3-propanediol (1 mole) was placed in a quart bottle and left in the refrigerator overnight. A reaction took place at once and a non-aqueous layer separated. This layer solidified on cooling, weight 136.4 g. It liquefied at room temperature and was dried over anhydrous sodium sulfate. Crude conversion was 72%. Attempted distillation of a portion of the product resulted in decomposition; m. p. of crystals, 32.0°. The remainder of the material was reduced and identified as the amine.

III. Hydrogenation of Nitro Amines to Polyamines[2]

The various nitro amines that were prepared were in turn hydrogenated to the corresponding polyamines. The method of reduction is illustrated in the following example:

One mole (146 g.) of N-(2-nitroisobutyl)-dimethylamine was dissolved in 500 ml. of methanol and 8 g. of Raney nickel catalyst added. The reduction was carried out at 30–50° under 500 lb. sq. in. of hydrogen. The completeness of the reduction may be followed by the absorption of hydrogen. The solution was filtered on removal from the bomb. The filtrate was distilled at room temperature to remove methanol. When nearly all the alcohol was removed, the distillation was stopped and 200 ml. of benzene added. A Dean and Stark moisture trap[3] was connected to the column and the mixture refluxed to remove water. (A binary constant boiling mixture of methanol and benzene distilled first.) Distillation of the residual product and benzene was then resumed, yielding 8 g. of material, b. p. 80–115° and 77 g. at 119° of the N-(2-aminoisobutyl)-dimethylamine. The residue was 5 g., conversion 66.5%.

The conversion to pure polyamines, on the basis of the nitroparaffins, was the same whether the pure nitro amines or the crude nitro amines were hydrogenated.

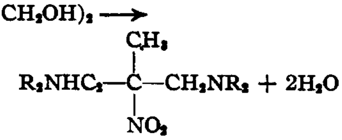
Acknowledgment.—The author wishes to thank Dr. J. A. Riddick, Dr. P. C. Markunas and associates for the analyses reported in this work.

Summary

The reaction of secondary aliphatic amines with formaldehyde and both primary and secondary nitroparaffins has been demonstrated. Two methods have been used to prepare the nitro amines either of which gives the same end-product, *e. g.*, the amine plus formaldehyde when treated with the nitroparaffin gives the nitro amine or the amine may be added directly to the nitro alcohol (or diol) to give the nitro amine. The reactions are illustrated as follows

$$R_2NH + CH_2O + (CH_3)_2CHNO_2 \longrightarrow R_2NCH_2C(CH_3)_2NO_2 + H_2O$$

$$2R_2NH + CH_3C(NO_2)(CH_2OH)_2 \longrightarrow$$



$$R_2NHC_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle NO_2}{C}}{-}CH_2NR_2 + 2H_2O$$

The nitro amines were reduced to the corresponding polyamines using Raney nickel catalyst.

TERRE HAUTE, INDIANA RECEIVED AUGUST 22, 1945

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[2] It is pointed out that hydrogenation of nitro amines to polyamines should not be started at high temperatures since a violent reaction may take place because of the exothermic nature of the hydrogenation process.

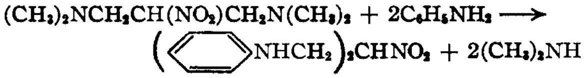
[3] Dean and Stark, *Ind. Eng. Chem.*, **12**, 486 (1920).

[CONTRIBUTION FROM RESEARCH AND DEVELOPMENT DEPARTMENT, COMMERCIAL SOLVENTS CORPORATION]

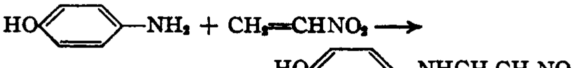
The Preparation and Reduction of Nitro Amines Obtained from Aromatic Amines, Formaldehyde, and Nitroparaffins*

BY HAL G. JOHNSON†

Duden, Bock and Reid[1] have shown that 2-nitro-1,3-bisanilinopropane can be prepared by the action of aniline on the reaction product of dimethylamine, formaldehyde and nitromethane. (According to our nomenclature the compound above would be N,N′-diphenyl-2-nitro-1,3-propanediamine.) It is to be noted, however, that the reaction is one of substitution



Dickey[2] has also shown the preparation of a number of compounds related in structure to those discussed in this paper. His compounds are prepared by the reaction of nitroolefins with amines.



All of the compounds prepared by this method must of necessity have at least one hydrogen atom alpha to the nitro group, *i. e.*, it is impossible to prepare a compound having both alpha hydrogen atoms substituted.

Cerf[3] stated that nitroparaffins of the type RCH_2NO_2 react with one mole of N-hydroxymethyldialkylamine. He was not successful in treating two moles, as did Henry,[4,5] Mousset[6] and Senkus,[7] all of whom obtained products of the type

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* Prepared for the 1945 Meeting-in-Print of the Division of Organic Chemistry, American Chemical Society.

† Presently associated with the Dykern Company, St. Louis, Missouri.

[1] Duden, Bock and Reid, *Ber.*, **38**, 2036 (1905).

[2] J. B. Dickey, U. S. Patent 2,292,212, October 5, 1939, "Amino Compound."

[3] Cerf, *Bull. soc. chim.*, [5] **4**, 1451 (1931); [5] **4**, 1460 (1931).

[4] Henry, *Ber.*, **38**, 2027 (1905).

[5] Henry, *Bull. acad. roy. med. Belgique*, [3] **33**, 412 (1897).

[6] Mousset, *ibid.*, 622 (1901).

[7] M. Senkus, THIS JOURNAL, **68**, 10 (1946).