β-Nitro-isobutyloxy-dihydro-*exo*-dicyclopentadiene.—Boron trifluoride–diethyl ether (40 g.) was added dropwise to a stirred solution of 178.5 g. of 2-nitro-isobutyl alcohol, 198 g. of dicyclopentadiene and 200 cc. of ethylene dichloride at 50°. The temperature was maintained at 50–55° by cooling with ice water. The time required for the addition was thirty minutes. After the exothermic reaction had ceased, the mixture was warmed for six hours at 40–50° then cooled, washed with water and dilute soda solution, followed by a water wash. The product after drying yielded 212 g. of the crude nitro ether as a colorless oil boiling at 160–180° (5 mm.). Upon refractionation this gave 169 g. of the pure product boiling at 136–137° (0.4 mm.).

Phenoxy-dihydro-*exo*-dicyclopentadiene.—To a stirred mixture of 132 g. of dicyclopentadiene and 94 g. of phenol there was added dropwise during the course of thirty minutes 18 g. of 98% sulfuric acid while the reaction mixture was maintained at 28–32° by a cold water-bath. The mixture was stirred thereafter for two hours, then poured into hot water. The oil layer was separated and washed thoroughly with hot water and soda solution. The washed oil was dried, mixed with 1% of its weight of dry sodium carbonate and distilled *in vacuo*. The fraction boiling at 140–150° (1 mm.) was a pale yellow oil. The yield was 98 g. On standing it solidified to a crystalline mass which after recrystallization from methanol with the aid of Norite formed colorless crystals, m. p. 70–71°.

Summary

1. Alcohols and phenols add to dicyclopentadiene in the presence of acidic catalysts (BF_3 or H_2SO_4) to yield rearranged unsaturated ethers, which are derivatives of hydroxy-dihydro-*exo*-dicyclopentadiene.

2. The lower aliphatic ethers thus obtained possess intense floral odors.

PHILADELPHIA, PENN. RECEIVED SEPTEMBER 5, 1945

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

Reaction of Primary Aliphatic Amines with Formaldehyde and Nitroparaffins*

BY MURRAY SENKUS

Henry[1,2] has shown that nitromethane reacts with N-hydroxymethyldimethylamine to give 2-nitro-1,3-bisdimethylaminopropane and with N-hydroxymethylpiperidine to give 2-nitro-1,3-bis-(N-piperidyl)-propane; also that N-hydroxymethylpiperidine reacts with nitroethane to give 2-nitro-2-methyl-1,3-bis-(N-piperidyl)-propane and with 3-nitro-1-propanol to give 2-nitro-2-(2-hydroxyethyl)-1,3-bis-(N-piperidyl)-propane. Mousset[3] allowed N-hydroxymethylpiperidine to react with 1-nitro-3-methylbutane and isolated 2-nitro-2-(2-methylpropyl)-1,3-bis-(N-piperidyl)-propane. Duden, Bock and Reid[4] repeated Henry's synthesis of 2-nitro-1,3-bisdimethylaminopropane and reduced the nitro amine with stannous chloride to 2-amino-1,3-bisdimethylaminopropane. They tried to condense N-hydroxymethylamine with nitromethane, but with no success. More recently Cerf[5] made an extensive study of the reaction of nitroparaffins with products derivable from aldehydes and amines and from formaldehyde and amides and on the basis of his work concluded that only 2 moles of a N-hydroxymethyldialkylamine will react with nitromethane and only one mole of a N-hydroxymethyldialkylamine will react with any other primary nitroparaffin. The latter conclusion was in contradiction to Henry's and Mousset's results. Cerf also concluded that N-hydroxymethyldialkylamines do not react with secondary nitroparaffins and that N-hydroxymethylmonoalkylamines do not react with either primary or secondary nitroparaffins.

In spite of the reports mentioned above which indicated that N-hydroxymethylisopropylamine would not react with 2-nitropropane, the reaction was tried. The two compounds reacted smoothly at room temperature to give N-(2-nitroisobutyl)-isopropylamine in 76% conversion. In view of this result the reactions of other N-hydroxymethylmonoalkylamines and other nitroparaffins were investigated and are reported in this paper.

It was also found that N-(2-nitroisobutyl)-isopropylamine can be prepared from 2-nitro-2-methyl-1-propanol and isopropylamine. Presumably the nitro alcohol in the presence of the amine yields 2-nitropropane and formaldehyde. The aldehyde and isopropylamine yield N-hydroxymethylisopropylamine which then reacts with 2-nitropropane as above. Some other nitro amines were prepared from primary amines and nitro alcohols derivable from nitroparaffins and formaldehyde and are reported in this paper.

The nitro amines which were prepared were hydrogenated to the corresponding polyamines. These hydrogenations are also described herein.

Experimental

I. Preparation of Some Nitro Amines from Secondary Nitroparaffins

Two methods were developed for the preparation of nitro amines from secondary nitroparaffins. These methods are described below and the preparation of N-(2-nitroisobutyl)-isopropylamine is used as an example.

Method A. From Isopropylamine, Formaldehyde and 2-Nitropropane.—Two moles of isopropylamine (118 g.) was placed in a two-liter, three-necked flask fitted with a condenser, a sealed stirrer, a dropping funnel and a thermometer reaching into the liquid. The flask was immersed in a water-bath, the temperature of which was maintained at 17–20°. Two moles of 36% (by weight) aqueous formaldehyde was added slowly to the flask while the mixture was agitated. The temperature of the mixture

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* Prepared for the September, 1945, Meeting-in-print.

(1) Henry, *Ber.*, **38**, 2027 (1905).

(2) Henry, *Bull. acad. roy. Belg.*, [3] **33**, 412 (1897).

(3) Mousset, *ibid.*, 622 (1901).

(4) Duden, Bock and Reid, *Ber.*, **38**, 2036 (1905).

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

TABLE I

SOME NITRO AMINES

F	Starting materials Amine	Starting materials Nitroparaffin	Product	Conversion	Method of prepn.	Boiling pt. °C.	Boiling pt. Mm.	$n^{20}D$	d^{20}_{20}	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
O R	Methylamine	2-Nitropropane	N-(2-Nitroisobutyl)-methylamine	48	A	60–62	6	1.4368	1.0166	$C_5H_{12}N_2O_2$	21.20	21.02
M A L	Isopropylamine	Nitroethane	2-Nitro-2-methyl-1,3-diisopropylaminopropane	71 60	A B	98–100	3	1.4518	0.9671	$C_{10}H_{23}N_3O_2$	19.34	19.31
D E	Isopropylamine	2-Nitropropane	N-(2-Nitroisobutyl)-isopropylamine	76 86	A B	84	10	1.4339	0.9685	$C_7H_{16}N_2O_2$	17.49	17.34
H Y D	Isopropylamine	1-Nitropropane	2-Nitro-2-ethyl-1,3-diisopropylaminopropane[b]									
E	Isopropylamine	2-Nitrobutane	N-(2-Nitro-2-methylbutyl)-isopropylamine	90	A	95–97	10	1.4409	0.9625	$C_8H_{18}N_2O_2$	16.08	16.09
	Butylamine	2-Nitropropane	N-(2-Nitroisobutyl)-butylamine	85	A	105–107	10	1.4407	0.9584	$C_8H_{18}N_2O_2$	16.08	15.95
	1-Methylpropylamine	2-Nitropropane	N-(2-Nitroisobutyl)-1-methylpropylamine	72	A	96	10	1.4384	0.9571	$C_8H_{18}N_2O_2$	16.08	16.17
	Benzylamine	2-Nitropropane	N-(2-Nitroisobutyl)-benzylamine	75	B	130–133	2	1.5178	1.0785	$C_{11}H_{16}N_2O_2$	13.45	13.59
	Benzylamine	Chloronitro methane	2-Nitro-2-chloro-1,3-dibenzylaminopropane	80	B	74.9[a]				$C_{17}H_{20}N_3O_2Cl$	10.62[c]	10.75[c]
	1-Phenylethylamine	2-Nitropropane	N-(2-Nitroisobutyl)-1-phenylethylamine	75	B	121–124	0.8	1.5080	1.0809	$C_{12}H_{18}N_2O_2$	12.60	12.85
	2-Amino-2-methyl-1-propanol	2-Nitropropane	N-(2-Nitroisobutyl)-2-amino-2-methyl-1-propanol	90	A	59.0[a]				$C_8H_{18}N_2O_3$	14.73	14.84
	2-Amino-1-butanol	2-Nitropropane	N-(2-Nitroisobutyl)-2-amino-1-butanol	10	A	58.1[a]				$C_8H_{18}N_2O_3$	14.73	14.49

[a] Melting point. [b] Purification of material was not attempted. Crude material was reduced to the polyamine. [c] Chlorine content.

TABLE II

SOME POLYAMINES

Polyamine	Boiling point °C.	Boiling point Mm.	$n^{20}D$	d^{20}_{20}	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
N-(2-Aminoisobutyl)-methylamine	123	750	1.4293	0.8149	$C_5H_{14}N_2$	27.42	27.38
2-Amino-2-methyl-1,3-diisopropylaminopropane	98–100	3	1.4502	.8596	$C_8H_{25}N_3$	22.43	22.35
N-(2-Aminoisobutyl)-isopropylamine	147.3	760	1.4263	.8025	$C_7H_{19}N_2$	21.51	22.06
2-Amino-2-ethyl-1,3-diisopropylaminopropane	71–72	1	1.4491	.8520	$C_9H_{27}N_3$	20.87	20.87
N-(2-Aminoisobutyl)-butylamine	64–66	10	1.4346	.8154	$C_8H_{20}N_2$	19.42	19.23
N-(2-Aminoisobutyl)-1-methylpropylamine	56–58	10	1.4297	.8171	$C_8H_{20}N_2$	19.42	19.41
N-(2-Amino-2-methylbutyl)-isopropylamine	57.5	10	1.4348	.8166	$C_8H_{20}N_2$	19.42	19.23
N-(2-Aminoisobutyl)-benzylamine	105–106	8	1.5153	.9526	$C_{11}H_{18}N_2$	15.71	15.52
N-(2-Aminoisobutyl)-1-phenylethylamine	110	5	....	.9373	$C_{12}H_{20}N_2$	14.57	14.37
N-(2-Aminoisobutyl)-2-amino-2-methyl-1-propanol	115–116	10	1.4651	.9360	$C_8H_{20}N_2O$	17.48	17.29
N-(2-Aminoisobutyl)-2-amino-1-butanol	118–121	10	1.4631	.9343	$C_8H_{20}N_2O$	17.48	17.05

was not allowed to exceed 25° during the addition of the aldehyde. Two moles of 2-nitropropane (178 g.) was added to the flask at one time and the mixture was stirred for thirty minutes without further cooling. Twenty grams of sodium sulfate was added to the mixture and stirring was continued until the salt had dissolved. The non-aqueous layer was separated from the water layer and was allowed to stand in the room for five days. A small additional amount of water separated from the crude product on standing. Distillation of this product through a four-foot laboratory column gave 25 g. of material, b. p. 34–85° at 10 mm. and 242 g. of N-(2-nitroisobutyl)-isopropylamine, b. p. 85° at 10 mm. The distillation was discontinued at this point because the residue (35 g.) began to decompose. Conversion to nitro amine was 76%.

Method B. From 2-Nitro-2-methyl-1-propanol and Isopropylamine.—One mole of isopropylamine (59 g.) and one mole of 2-nitro-2-methyl-1-propanol (119 g.) were placed in a glass-stoppered bottle and the mixture was shaken until it had become homogeneous. The solution was allowed to stand at room temperature. Water began to separate as a lower layer after ten hours. The separation of water ceased after three days. The top layer was distilled through a column at reduced pressure. Conversion to nitro amine was 86%.

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

Two methods were developed for the preparation of nitro diamines from primary amines, formaldehyde and primary nitroparaffins. The preparation of 2-nitro-2-methyl-1,3-diisopropylaminopropane according to each of those methods is described below for illustration.

Method A. From Isopropylamine, Formaldehyde and Nitroethane.—Two moles of isopropylamine and two moles of formaldehyde were mixed as above. One mole of nitroethane (75 g.) was added to the mixture with agitation over thirty minutes. Twenty grams of sodium sulfate was added and stirring was continued until the salt had dissolved. The non-aqueous layer was separated from the water layer and was allowed to stand over 5 g. of anhydrous sodium sulfate for three days. The mixture was 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:

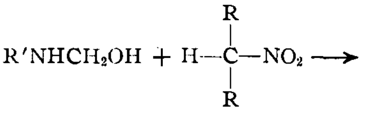
One hundred grams of nitroamine (either pure nitroamine or crude nitroamine which had not been rectified) was dissolved in 100 ml. of methanol and the solution was hydrogenated at 30–50° and 500 lb./sq. in. in the presence of 5 g. of Raney nickel. The solution was filtered and the filtrate was distilled 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.

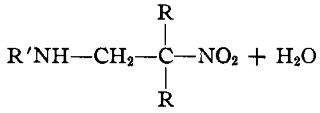
Lists of nitroamines and polyamines prepared together with some of their properties are given in Tables I and II.

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

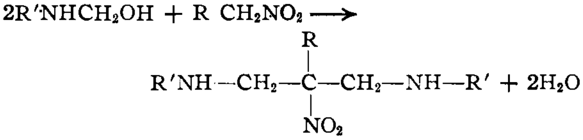


$$R'NHCH_2OH + H-\overset{R}{\underset{R}{C}}-NO_2 \longrightarrow$$



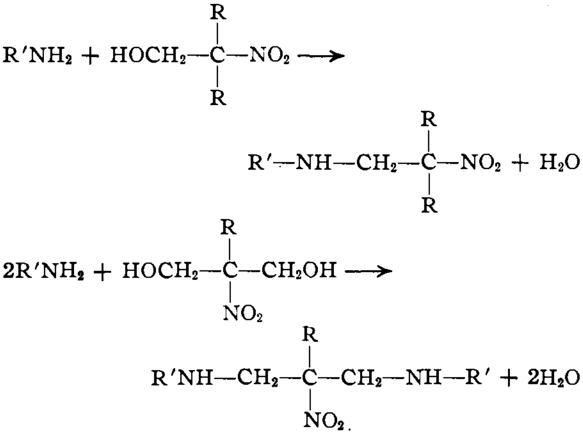
$$R'NH-CH_2-\overset{R}{\underset{R}{C}}-NO_2 + H_2O$$

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



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

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



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

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

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.