

The Utilization of Aliphatic Nitro Compounds IX. Preparation and Properties of Aliphatic Nitroalcohols and Aminoalcohols*

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During the past few years the nitroparaffins have become available in quantities sufficiently large to permit a thorough investigation of their properties. Hass and Vanderbilt (1) studied the condensation of aldehydes with nitroparaffins, and Degering and Johnson (2) investigated the reduction of nitroalcohols to the corresponding amino compounds.

The work reported in this paper is a continuation of both the nitroparaffin-aldehyde condensation and the reduction of nitroparaffins with respect to the production of four nitroalcohols and the corresponding aminoalcohols. The nitroalcohols prepared and studied are: (1) 2-methyl-2-nitro-3-pentanol, (2) 2-methyl-2-nitro-3-hexanol, (3) 3-methyl-3-nitro-4-heptanol, and (4) 2-nitro-1-hexanol. These compounds were prepared by the use of formaldehyde, propionaldehyde, or butyraldehyde with 1-nitropropane, 2-nitropropane, 2-nitrobutane, and 1-nitropentane.

1. *Condensation product of 2-nitropropane: 2-Methyl-2-nitro-3-pentanol.*

Into a 500 ml. three-necked flask, equipped with a mercury seal and a motor-driven stirrer, were placed 89 g. (1 mol) of 2-nitropropane, 25 ml. of 95% ethyl alcohol, and 4 ml. of 10 N sodium hydroxide. Then 60.9 g. (1 mol + 5% x's) of propionaldehyde, at slightly below room temperature, was added dropwise with vigorous agitation. Addition of the aldehyde was complete in about 40-50 minutes. Five milliliters of water was added to give a clear solution. The solution was allowed to stand six days at room temperature, and the alkali then neutralized with an equivalent amount of hydrochloric acid. The precipitated sodium chloride was filtered off, and the ethyl alcohol stripped from the solution at 30 mm. pressure (water pump). Additional sodium chloride, which precipitated during this operation, was filtered off and the solution fractionated under vacuum on a modified Podbielniak column. The conversion was 46-52%, based upon the quantity of 2-nitropropane used. The boiling point was 94.5° C. at 10 mm. pressure. The crude nitroalcohol was washed with 10 ml. of 33 1/3% sodium bisulfite solution, dried with anhydrous magnesium sulfate, and redistilled. The nitroalcohol thus obtained was almost water-white.

2. *Condensation product of 1-nitropentane: 2-nitro-1-hexanol.*

1-Nitropentane was condensed with formaldehyde, the best of two runs giving a 73% conversion, based upon the 1-nitropentane. High yields are ordinarily obtained with a primary nitroparaffin.

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These four nitroalcohols prepared by this nitroparaffin-aldehyde condensation have the physical constants listed in Table I.

Table I—Physical Constants of Some Nitroalcohols

Nitroalcohol	Prepared from	B.P.° C.	Specific Gravity 25° C.	Refractive Index 20° C.
2-methyl-2-nitro-3-hexanol	2-Pr.NO ₂ +C ₃ H ₇ CHO	86.5 at 5 mm.	1.0435	1.4494
3-methyl-3-nitro-4-heptanol	2-Bu.NO ₂ +C ₃ H ₇ CHO	117 at 10 mm.	1.0281	1.4534
2-methyl-2-nitro-3-pentanol	2-Pr.NO ₂ +C ₂ H ₅ CHO	94.5 at 10 mm.	1.0748	1.4488
2-nitro-1-hexanol	1-Am.NO ₂ +HCHO	102.9 at 5 mm.	1.0556	1.4451

In order to obtain the nitroalcohols in maximum yields, the aldol polymerization must be suppressed. All the aliphatic aldehydes possessing *alpha* or (4-position) hydrogen atoms undergo this latter reaction with ease, necessitating some means of keeping the extent of this polymerization at a minimum. Since both the nitroparaffin-aldehyde condensation and aldol polymerization take place in an alkaline medium, they are completing reactions. The aldol polymerization may be minimized by keeping the reaction mixture in a homogeneous state at all times. The volume of solvent alcohol used should be sufficient to insure this homogeneity. The aldehyde must be added in such a manner that there will be an excess of nitroparaffin in the reaction mixture at all times. Before recovering the nitroalcohol from the reaction mixture, the alkali should be carefully neutralized. By observation of these precautions, the formation of the aldol-type products may be minimized.

During the recovery of the nitroalcohol, nitroolefins may be produced. This reaction takes place by the elimination of a molecule of water from the nitroalcohol:



This undesirable side reaction may be avoided in general by working at lower temperatures. Nitroolefins have distinct lachrymatory properties and are easily polymerized to highly colored substances.

Reduction of the Nitroalcohols to the Corresponding Aminoalcohols

The nitroalcohols made, with one exception, were hydrogenated to the aminoalcohols. These products should have properties similar to those of the ethanolamines and, consequently, have commercial application. Degering and Johnson (2) hydrogenated nitroglycols and nitroalcohols, but no attempt was made to purify the reduction products obtained from the nitroalcohols, which contained less than six carbon atoms. It has been found that the nitroalcohols are unstable under most reducing conditions (1, 2).

The apparatus used for this part of the work was a bomb built by the Parr Instrument Company. It was of 500 ml. of capacity and was

capable of withstanding a pressure of 6,000 pounds per square inch. The reductions were carried out at room temperature, the bomb being rocked at the rate of thirty times per minute. The hydrogen was obtained from an industrial cylinder (2,000 pounds pressure or less).

The catalyst is prepared by treating powdered Raney alloy (50% Ni and 50% Al) with 25% sodium hydroxide to dissolve the aluminum. The next step consists in washing the catalyst with water until the solution is no longer basic to phenolphthalein. A final wash is made with 45% ethanol. The amount of catalyst weighed out for each run is twice the weight desired, due to removal of half the weight by solution in sodium hydroxide.

The nitroalcohol, solvent alcohol, and catalyst are placed in the bomb, and the mixture is shaken at the desired hydrogen pressure. When the pressure becomes constant for a period of an hour, showing that no further hydrogenation is taking place, the agitation is discontinued. The catalyst is filtered from the solution and an aliquot portion titrated with standard acid to determine conversion to base. After fractionation, the aminoalcohol is dried with anhydrous potassium carbonate and redistilled. Table II summarizes the physical constants of the three aminoalcohols produced.

TABLE II.

Aminoalcohol	B. P. °C.	Specific Gravity	Refractive
		26° C.	Index 20° C.
2-Amino-2-methyl-3-pentanol	50 at 4 mm.	0.9824	1.4508
2-Amino-2-methyl-3-hexanol	63.5 at 5 mm.	0.9782	1.4461
3-Amino-3-methyl-4-heptanol	98 at 4¼ mm.	0.9810	1.4366

Although the conversions to base were high (85-93%), the yields of aminoalcohols obtained were low, the highest being 31%.

The aminoalcohols obtained are viscous, high boiling, water-white liquids, possessing an odor much less penetrating than that of an aliphatic amine or ammonia.

Summary

Certain nitroparaffins have been condensed with certain aliphatic aldehydes in a basic solution to give the aliphatic nitroalcohols.

The nitroalcohols so formed have been reduced to the corresponding aminoalcohols by catalytic hydrogenation.

The compounds prepared were: 2-methyl-2-nitro-3-hexanol, 3-methyl-3-nitro-4-heptanol, 2-methyl-2-nitro-3-pentanol*, 2-nitro-1-hexanol*, 2-amino-2-methyl-3-hexanol*, 3-amino-3-methyl-4-heptanol*, 2-amino-2-methyl-3-pentanol*. The starred compounds represent new composition of matter.

References

- Vanderbilt and Hass, *Ind. Eng. Chem.*, **32**:34. 1940.
- Johnson, Ph.D. Thesis, Purdue University (1937); Degering and Johnson, *J. Am. Chem. Soc.* **61**:3194. 1935.