Aldehyde-Nitroparaffin Condensation[1]

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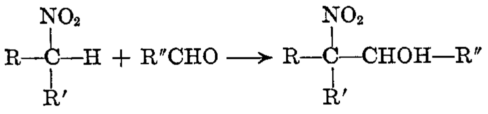
Although the aldehyde-nitroparaffin condensation to give nitroalcohols has been known for over forty years, many of the simple aliphatic nitroalcohols had not been prepared until this investigation was undertaken. Recent developments in vapor-phase nitration have made the lower aliphatic nitroparaffins available (*3*). By means of condensations of nitroethane, the nitropropanes, and the nitrobutanes with formaldehyde, acetaldehyde, and butyraldehyde, respectively, a number of monohydric and dihydric alcohols have been prepared. Typical acetates of these alcohols have been synthesized. Reduction of the nitroalcohols gives the corresponding aminoalcohols. The physical and chemical properties of the various compounds prepared are given. Certain theoretical aspects of their preparation are discussed. Some possible commercial uses are suggested.

VICTOR MEYER, the discoverer of the nitroparaffins, recognized that the hydrogen atoms attached to the nitro-bound carbon atom of primary or secondary nitroparaffins had properties different from those attached to other carbon atoms in the nitroparaffin molecule. However, it was not until twenty-three years later that Henry (*4*) discovered that nitroalcohols could be prepared from nitroparaffins by condensation with aliphatic aldehydes. From 1895 to 1902 Henry and his co-workers—Maas, Mousset, Pauwels, and Shaw—prepared a number of nitroalcohols by condensing aldehydes with nitroparaffins. They studied some of the properties and prepared a few derivatives. However, the literature is incomplete and in some cases conflicting relative to the preparation and properties of the nitroalcohols which may be obtained from the lower nitroparaffins and the more common aliphatic aldehydes.

In order to make a systematic study of this condensation reaction, nitroethane, 1-nitropropane, 2-nitropropane, 1-nitrobutane, 2-nitrobutane, and 2-methyl-1-nitropropane were condensed with formaldehyde, acetaldehyde, and butyraldehyde, respectively. Nitromethane was omitted because it had previously been studied thoroughly (*4, 7*). The six nitroparaffins employed can readily be obtained by vapor-phase nitration of the corresponding hydrocarbons (*3*). The three aldehydes used are inexpensive articles of commerce.

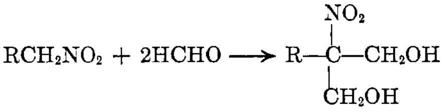
Methods of Preparing Nitroalcohols

The general reaction for the aldehyde-nitroparaffin condensation is as follows:



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

In case the nitroparaffin is primary and the aldehyde is formaldehyde, two molecules of aldehyde react:



$$RCH_2NO_2 + 2HCHO \longrightarrow R{-}\underset{CH_2OH}{\overset{NO_2}{C}}{-}CH_2OH$$

Unlike most aldehyde condensations, the aldehyde-nitroparaffin reaction does not occur unless the mixture is definitely alkaline. In order to obtain good yields of the nitroalcohols, aldol and polymer formation from the aldehydes employed had to be kept to a minimum. Since alkaline reagents are also catalysts for the formation of these latter substances, it was necessary to adopt experimental conditions unfavorable to their formation. Another undesirable reaction which may occur during the aldehyde-nitroparaffin reaction and recovery of the product, is the formation of nitroölefins and their polymers. A nitroalcohol derived from a primary nitroparaffin may split off water to form the corresponding nitroölefin:

$$RCHNO_2CHOHR' \longrightarrow RCNO_2{=}CHR' + H_2O$$

When nitroalcohols are prepared from aromatic aldehydes, this type of reaction is difficult to avoid (*8*). When nitroalcohols are prepared from aliphatic aldehydes and primary nitroparaffins, the formation of nitroölefins may be avoided completely by not using elevated temperatures until the reaction mixture has been neutralized. Nitroölefins are particularly undesirable since they are strong lachrymators and polymerize to highly colored products. By following the rules of procedure listed, the formation of aldols, nitroölefins, and polymers is kept to a minimum:

1. Use the minimum concentration of catalyst to obtain a reasonable reaction velocity.
2. Keep the reaction mixture homogeneous at all times, preferably by maintaining one phase.

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[1] This is the ninth in a series on the subject of syntheses from natural gas hydrocarbons. The others appeared in INDUSTRIAL AND ENGINEERING CHEMISTRY: **23**, 352 (1931); **27**, 1190 (1935); **28**, 333, 339, 1178 (1936); **29**, 1335 (1937); **30**, 67 (1938); **31**, 118 (1939).

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3. Regulate the temperature to a practical minimum.
4. Maintain a molal excess of the nitroparaffin at all times.
5. Remove the alkaline catalyst quantitatively before working up the reaction mixture.

The pure nitroparaffins used in the various syntheses were obtained by careful rectification of the crude nitration products of propane or one of the butanes. 1-Nitropropane, 1-nitrobutane, 2-nitrobutane, and 2-methyl-1-nitropropane were obtained from the nitration products of the corresponding hydrocarbons. In the nitration of propane, both nitroethane and 2-nitropropane are formed along with nitromethane and 1-nitropropane (*3*). However, as nitroethane and 2-nitropropane distill so closely (113° and 118° C., respectively), it was not practical to try to obtain either of these two nitroparaffins in a pure state from this mixture. Nitromethane, nitroethane, 1-nitropropane, 2-nitrobutane, and 1-nitrobutane are formed when nitrating *n*-butane. Pure nitroethane was easily obtained from this mixture. In the nitration of isobutane, 2-nitropropane is formed with no nitroethane so that the nitration product from this hydrocarbon was used for the isolation of pure 2-nitropropane.

The formaldehyde employed was Mallinckrodt's U. S. P. grade. The acetaldehyde and butyraldehyde were commercial products which were carefully rectified. Each was freshly distilled prior to use in order to free the aldehyde from any aldol and/or oxidation products.

The following examples illustrate the technique employed in the preparation of the mono- and dihydric nitroalcohols:

5-NITRO-4-OCTANOL. Into a 500-cc. three-neck flask were placed 206 grams of 1-nitrobutane (2 moles), 100 cc. of 95 per cent alcohol, and 4 cc. of 10 *N* sodium hydroxide solution. One hundred and forty-four grams of freshly distilled butyraldehyde (2 moles) were added slowly to the well-agitated solution. Reaction temperature was maintained at 30–35° C. by external cooling. When approximately two thirds of the butyraldehyde had been added, an additional 4 cc. of 10 *N* sodium hydroxide and 15 cc. of water were added. After addition of the aldehyde was complete, the solution was allowed to stand at 35–38° for 4 days. The alkali was neutralized with an equivalent amount of hydrochloric acid and the mixture distilled under slightly reduced pressure. A small amount of unreacted butyraldehyde distilled with the ethyl alcohol followed by a little 1-nitrobutane and higher boiling impurities. The pressure was finally reduced to 5 mm. and the 5-nitro-4-octanol distilled. It was obtained as a pale yellow liquid. The yield was 310 grams (88.5 per cent of theory, based upon the 1-nitrobutane and the butyraldehyde employed).

2-ETHYL-2-NITRO-1,3-PROPANEDIOL. Into a 500-cc. three-neck flask were placed 35.6 grams of 1-nitropropane (0.4 mole) and 0.1 gram of hydrated lime. Sixty-four grams of 37.5 per cent formalin solution (0.8 mole of formaldehyde) were added dropwise to the well-stirred mixture. During the addition the temperature rose to 30° C. and was prevented from going higher by external cooling with tap water. On addition of approximately half of the formalin, the contents of the flask became one phase. After addition was complete and the exothermic reaction had subsided, the solution was allowed to stand at room temperature for 43 hours. Carbon dioxide in very slight excess was added and the calcium carbonate removed by means of a Filter-Cel suction filter. The precipitate was washed with 5 cc. of water, and the combined filtrate and washings were evaporated at 200 mm. The residue was finally heated to 90° at 20 mm. in a water bath. The molten product which remained in the distilling flask solidified on cooling. Yield was 59.4 grams of 2-ethyl-2-nitro-1,3-propanediol, of 98–99 per cent purity, practically a theoretical yield.

Purification and Properties of Nitroalcohols

The four nitroglycols (from the four primary nitroparaffins employed), 2-methyl-2-nitro-1-propanol, and 2-methyl-3-nitro-4-heptanol are solids at room temperature. The nitroglycols were obtained as solid residues on evaporation of their mother liquors and subsequent cooling. They were 95–99 per cent pure as obtained. Their chief impurities were paraformaldehyde and the corresponding monohydric nitroalcohols. They were purified by crystallization from a hot benzene-butanol solution and from water. The two solid monohydric alcohols may be purified by vacuum distillation and/or crystallization. A naphtha and benzene solution was used for crystallizing 2-methyl-2-nitro-1-propanol, and naphtha for 2-methyl-3-nitro-4-heptanol.

All the liquid nitroalcohols were colored yellow when obtained by vacuum distillation of the reaction mixture. They were aerated at 75–100° C. for about half an hour in order to hasten the polymerization of any unsaturates and then were washed with saturated sodium bisulfite solution to remove any aldehydes. Subsequent fractionation through a modified Podbielniak column at 10 mm. sufficed to convert them to colorless or nearly colorless products.

The solids are all white crystalline substances whose crystals suggest those of inorganic salts. The liquids are somewhat viscous and have a faint but rather sharp odor. All the dihydric nitroalcohols and those monohydric nitroalcohols containing less than seven carbon atoms are quite soluble in water. The former are insoluble in nonbenzenoid hydrocarbons as are the monohydric nitroalcohols containing less than six carbon atoms. All of these nitroalcohols are stable up to 100° C. but unstable at temperatures of 150° or above. They have chemical properties characteristic of aliphatic alcohols and nitroparaffins. Their chemical activity varies with the individual compounds. Table I summarizes some of their physical constants.

Aminoalcohols from Nitroalcohols

Nitroalcohols may be reduced to the corresponding aminoalcohols. Piloty and Ruff (*12*) reduced 2-methyl-2-nitro-1,3-propanediol with tin and hydrochloric acid to obtain impure 2-amino-2-methyl-1,3-propanediol. Their product melted at 60–95° C. Henry (*6*) used iron and acetic acid for reducing some of the nitroalcohols which he had prepared to the corresponding amino compounds. In all cases yields were low when metals were used in acids for such reductions. Montmollin and Achermann (*9*) state that this is due to the "fragility" of the aminoalcohols. They obtained a 50 per cent yield of 1-amino-2-butanol when 1-nitro-2-butanol was reduced with aluminum amalgam in alcohol.

It is believed that Schmidt and Wilkendorf (*13*) are the only investigators who previously had used catalytic hydrogenation for preparing aminoalcohols from nitroalcohols. They employed palladium as catalyst in an oxalic acid solution. They state that poor results are obtained when using neutral or alkaline solution.

The four nitroglycols cited in Table I were catalytically hydrogenated over Raney nickel (*1*) in collaboration with K. Johnson.[3] When pure, these dihydric aminoalcohols are solids at room temperature and cannot be distilled at atmospheric pressure without decomposition. They were obtained as viscous yellow sirups or gray-yellow solids. 2-Amino-2-methyl-1,3-propanediol was purified by crystallization from acetone. It was very difficult to get 2-amino-2-ethyl-1,3-propanediol as a solid. The crude reduction product was distilled at 1 mm. with slight decomposition. The distillate was placed in a refrigerator, and 23 days passed be-

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[3] This process will be described in detail in a later paper to be published from this laboratory

TABLE I. PHYSICAL CONSTANTS OF NITROALCOHOLS

Nitroalcohol	Prepared from		B. P. at 10 Mm., ° C.	Specific Gravity, d_4^{25}	Refractive Index, n_D^{20}	% Nitrogen	
	Nitroparaffin	Aldehyde				Theoretical	Found
2-Nitro-1-propanol	$EtNO_2$	HCHO	99	1.1841	1.4379	...	....
3-Nitro-2-butanol	$EtNO_2$	CH_3CHO	92	1.1296	1.4420	...	....
2-Nitro-3-hexanol	$EtNO_2$	C_3H_7CHO	108	1.0575	1.4480	9.52	9.42, 9.45
2-Nitro-1-butanol	$1\text{-}PrNO_2$	HCHO	105	1.1332	1.4390	...	....
3-Nitro-2-pentanol	$1\text{-}PrNO_2$	CH_3CHO	100	1.0818	1.4419	...	....
3-Nitro-4-heptanol	$1\text{-}PrNO_2$	C_3H_7CHO	115	1.0275	1.4460	8.70	8.65, 8.72
2-Methyl-2-nitro-1-propanol	$2\text{-}PrNO_2$	HCHO	89.5–90[a]	....	....	...	....
3-Methyl-3-nitro-2-butanol	$2\text{-}PrNO_2$	CH_3CHO	90	1.1021	1.4469	10.53	10.58, 10.72
2-Methyl-2-nitro-3-hexanol	$2\text{-}PrNO_2$	C_3H_7CHO	109	1.0405	1.4499	8.70	8.55, 8.69
2-Nitro-1-pentanol	$1\text{-}BuNO_2$	HCHO	117	1.0818	1.4405	...	....
3-Nitro-2-hexanol	$1\text{-}BuNO_2$	CH_3CHO	112	1.0487	1.4438	...	....
5-Nitro-4-octanol	$1\text{-}BuNO_2$	C_3H_7CHO	124	1.0394	1.4463	8.00	7.81, 7.94
2-Methyl-2-nitro-1-butanol	$2\text{-}BuNO_2$	HCHO	98	1.1047	1.4468	10.53	10.51, 10.53
3-Methyl-3-nitro-2-pentanol	$2\text{-}BuNO_2$	CH_3CHO	100	1.1157	1.4518	9.52	9.39, 9.42
3-Methyl-3-nitro-4-heptanol	$2\text{-}BuNO_2$	C_3H_7CHO	119	1.0281	1.4532	8.00	7.81, 7.93
3-Methyl-2-nitro-1-butanol	$1\text{-}Iso\text{-}BuNO_2$	HCHO	111	1.0886	1.4430	...	....
4-Methyl-3-nitro-2-pentanol	$1\text{-}Iso\text{-}BuNO_2$	CH_3CHO	96–98	1.0599	1.4477	...	....
2-Methyl-3-nitro-4-heptanol	$1\text{-}Iso\text{-}BuNO_2$	C_3H_7CHO	111	1.0140	1.4485	8.00	7.98, 8.11
2-Methyl-3-nitro-4-heptanol (stereoisomer)	$1\text{-}Iso\text{-}BuNO_2$	C_3H_7CHO	121 (53[a])	....	....	8.00	7.91, 8.12
2-Methyl-2-nitro-1,3-propanediol	$EtNO_2$	2HCHO	149–150[a]	....	....	...	....
2-Ethyl-2-nitro-1,3-propanediol	$1\text{-}PrNO_2$	2HCHO	56[a]	....	....	...	....
2-Nitro-2-propyl-1,3-propanediol	$1\text{-}BuNO_2$	2HCHO	81–81.5[a]	....	....	...	....
2-Nitro-2-isopropyl-1,2-propanediol	$1\text{-}Iso\text{-}BuNO_2$	2HCHO	87–88[a]	....	....	...	....
2-Amino-2-ethyl-1,3-propanediol	....	......	.....	....	....	11.76	11.56, 11.69
2-Amino-2-propyl-1,3-propanediol	....	......	.....	....	....	10.52	10.25, 10.32
2-Amino-2-isopropyl-1,3-propanediol	....	......	.....	....	....	10.52	10.35, 10.38

[a] Melting point.

fore it solidified to a waxlike solid. A portion of this was then crystallized from butanol-toluene solution several times. It was necessary to cool to 0° C. and seed in order to obtain crystallization. Due to the amorphous nature of this product the last of the solvents could not be expelled by drying so that the recrystallized material was again distilled under vacuum to remove the last of the solvents. The liquid distillate was solidified by seeding and was used as such for analysis and determination of melting point. 2-Amino-2-propyl-1,3-propanediol was obtained pure by distillation at 1 mm. 2-Amino-2-isopropyl-1,3-propanediol crystallized nicely from benzene-butanol solution.

The dihydric aminoalcohols are all solids at room temperature and have a mild amine odor. They are much more stable thermally than are the corresponding nitroalcohols. They are stable toward strong alkalies at ordinary temperatures and form salts with acids.

The melting points of these aminoalcohols (in ° C.) are as follows:

2-Amino-2-methyl-1,3-propanediol	108–109
2-Amino-2-ethyl-1,3-propanediol	37.5–38.5
2-Amino-2-propyl-1,3-propanediol	58
2-Amino-2-isopropyl-1,3-propanediol	74

Acetates of Nitroalcohols

The only organic esters of these nitroalcohols which had been prepared previous to this investigation were the acetates of 2-nitro-1-butanol and 3-methyl-2-nitro-1-butanol. The former was prepared by Pauwels (*11*) from acetic anhydride and the corresponding alcohol and is described as a yellow liquid having a penetrating odor, as being easy to saponify, and as having a boiling point of 130° C. at 35 mm. The latter was prepared by Shaw (*15*), and its boiling point is given as 159–168° C. (38 mm.).

In order to observe the general properties of such compounds, the acetates of four typical nitroalcohols were prepared. Those esterified were:

2-Nitro-1-butanol, a primary alcohol whose nitro group is attached to a secondary carbon atom.

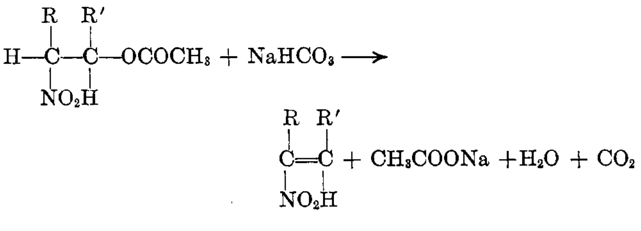
2-Methyl-2-nitro-1-butanol, a primary alcohol whose nitro group is attached to a tertiary carbon atom.

3-Nitro-2-butanol, a secondary nitroalcohol.

2-Ethyl-2-nitro-1,3-propanediol, a typical nitroglycol.

The standard procedure for preparing acetates from acetic anhydride was followed in the preparation of these esters. They were washed only with water prior to distillation. Nearly theoretical yields were obtained. The esters were further purified by rectification at 10 mm.

These acetates are all clear, colorless liquids with a faint, slightly mustardlike odor. Those from the monohydric alcohols are less viscous than the alcohols from which they are derived. All are less than one per cent soluble in water. They are thermally stable at 95° C., but at 150° the acetates of 2-nitro-1-butanol and 3-nitro-2-butanol became discolored within 5 hours; those of 2-methyl-2-nitro-1-butanol and 2-ethyl-2-nitro-1,3-propanediol showed no change after being heated at 150° C. for 16 hours. Similarly, the two esters in which the nitro group is attached to a tertiary carbon atom—i. e., the acetates of 2-methyl-2-nitro-1-butanol and 2-ethyl-2-nitro-1,3-propanediol—are very stable toward mild hydrolytic agents. However, the two acetates in which the nitro group is attached to a secondary carbon atom are very reactive toward all hydrolytic agents. It was found that boiling water rapidly decomposed the acetates of 2-nitro-1-butanol and 3-nitro-2-butanol. Sodium bicarbonate (0.1 *N*) decomposes such compounds and liberates the corresponding nitroolefin and sodium acetate:



$$\mathrm{H{-}\overset{R}{\underset{NO_2}{C}}{-}\overset{R'}{\underset{H}{C}}{-}OCOCH_3} + \mathrm{NaHCO_3} \longrightarrow \overset{R}{\underset{NO_2}{C}}{=}\overset{R'}{\underset{H}{C}} + \mathrm{CH_3COONa} + \mathrm{H_2O} + \mathrm{CO_2}$$

Thus the instability of such esters is not a matter of hydrolysis but is rather a cleavage of the ester molecule. The common physical constants of these esters are as follows:

	B. P. at 10 Mm., ° C.	Specific Gravity, d_4^{25}	Refractive Index, n_D^{20}
Acetate of 2-nitro-1-butanol	103	1.1164	1.4287
Acetate of 3-nitro-2-butanol	103	1.1089	1.4281
Acetate of 2-methyl-2-nitro-1-butanol	109	1.0932	1.4350
Diacetate of 2-ethyl-2-nitro-1,3-propanediol	157	1.1718	1.4444

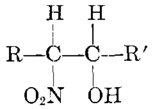
Identification of New Compounds

In all of the aldehyde-nitroparaffin condensations carried out, the normal course of reaction as reported by Henry and others evidently occurred. In no case did rearrangement take place. Those compounds described above which had not previously been reported were identified by analyses.

The monohydric nitroalcohols were analyzed for nitrogen by the method of Dumas. Some difficulty was encountered owing to the tendency of the sample to oxidize too rapidly in the combustion furnace and thus to give results which were too high. This difficulty was overcome by mixing the sample with a fifty-fifty mixture of copper oxide and calcium carbonate rather than with pure copper oxide. The dihydric nitroalcohols were analyzed for nitrogen by reducing to amino compounds, followed by regular Kjeldahl analysis. A 0.35-gram sample of nitroalcohol, 0.75 gram of aluminum dust, and 8 mg. of mercuric chloride were heated in dilute sulfuric acid in a Kjeldahl flask on the steam bath. After reduction was complete, the acid was concentrated by boiling, and the regular Kjeldahl digestion and analysis were carried out. The monohydric nitroalcohols gave low results by this method. The aminoalcohols were analyzed for nitrogen by the Kjeldahl method. The acetates were analyzed for nitrogen by the Dumas method. Table I summarizes the analyses of new compounds.

Stereoisomerism

Optical stereoisomers are possible for all the monohydric nitroalcohols prepared with the exception of 2-methyl-2-nitro-1-propanol. Any nitroalcohol obtained from an aldehyde higher than formaldehyde and a primary nitroparaffin other than nitromethane, gives a compound of the following type formula:



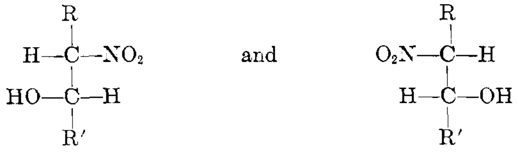
$$\begin{array}{ccccc} & \text{H} & & \text{H} & \\ & | & & | & \\ \text{R}- & \text{C} & - & \text{C} & -\text{R}' \\ & | & & | & \\ & \text{O}_2\text{N} & & \text{OH} & \end{array}$$

Regardless of whether R and R′ are alike or not, such a molecule contains two asymmetric carbon atoms. Furthermore, the molecule is unsymmetrical. By means of the formula

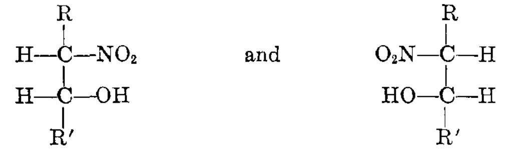
$$N = 2^n$$

where N = number of stereoisomers
n = number of asymmetric carbon atoms

one can predict two dextro and two levo forms—i. e., two racemic isomers. They are represented by the following projection formulas:



$$\begin{array}{c} \text{R} \\ | \\ \text{H}-\text{C}-\text{NO}_2 \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{R}' \end{array} \quad \text{and} \quad \begin{array}{c} \text{R} \\ | \\ \text{O}_2\text{N}-\text{C}-\text{H} \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{R}' \end{array} \qquad (1)$$



$$\begin{array}{c} \text{R} \\ | \\ \text{H}-\text{C}-\text{NO}_2 \\ | \\ \text{H}-\text{C}-\text{OH} \\ | \\ \text{R}' \end{array} \quad \text{and} \quad \begin{array}{c} \text{R} \\ | \\ \text{O}_2\text{N}-\text{C}-\text{H} \\ | \\ \text{HO}-\text{C}-\text{H} \\ | \\ \text{R}' \end{array} \qquad (2)$$

These racemic forms should possess somewhat different physical properties. They would be optically inactive, but each could be divided into its respective dextro and levo forms by the known methods. Likewise a nitroalcohol derived from an unsymmetrical secondary nitroparaffin and an aldehyde other than formaldehyde can exist as two optically inactive isomers—e. g., 3-methyl-3-nitro-2-pentanol.

From the properties of most of the nitroalcohols prepared which contain two asymmetric carbon atoms, it was apparent that only one of the racemic isomers was formed or that the two had nearly identical boiling points. However, the two nitroalcohols derived from 2-methyl-1-nitropropane and acetaldehyde and butyraldehyde, respectively, were exceptions. Both of these compounds distilled over a definite boiling range. That from butyraldehyde and 2-methyl-1-nitropropane had a sufficiently wide boiling range so that the two isomers could be separated to a large degree by careful rectification. One of these proved to be a solid at ordinary temperature which greatly facilitated further separation.

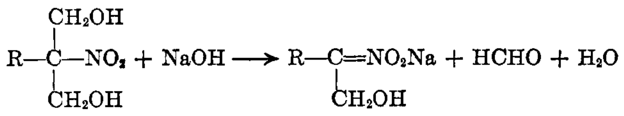
The condensation product of two moles of 2-methyl-1-nitropropane and two moles of butyraldehyde was carefully fractionated at 10 mm. Approximately 60 per cent of the 2-methyl-3-nitro-4-heptanol was obtained at about 111° C., and 40 per cent distilled close to 121°. The former was further purified by refractionation and the latter by crystallization from pentane. A portion of each was reduced to the corresponding aminoalcohols, and they were found to have different physical constants. The acetates were also prepared and were found to be different. The analytical data showed both of the compounds to have the composition of 2-methyl-3-nitro-4-heptanol:

	Solid Isomer	Liquid Isomer
Nitrogen by Dumas method (theory 8.00), %	7.91, 8.12	7.98, 8.11
Nitrogen of acetate by Dumas (theory 6.45), %	6.41, 6.51	6.39, 6.45
Nitrogen of aminoalcohol by titration (theory 9.65), %	9.26	9.36
Molecular weight (theory 175.1)	177.3	175.1
Boiling point at 10 mm., ° C.	121	111
Melting point, ° C.	53	....
Boiling point of acetate at 10 mm., ° C.	122.5	128

Discussion

Aliphatic aldehydes undergo several condensation reactions other than those with nitroparaffins. The addition compounds with sodium bisulfite, ammonia, and hydrogen cyanide are well known. As previously stated, the nitroparaffins, unlike the compounds mentioned above, do not spontaneously condense with aldehydes, but the reaction must be promoted by a definite type of catalyst. Previous investigators used a variety of alkaline catalysts, including alkali carbonates and hydroxides, sodium methylate and ethylate, methylamine, ethylamine, amylamine, piperidine, sodium sulfite, sodium acetate, and borax. We have used similar catalysts but not ammonia, primary amines, or secondary amines because of their reactivity toward aldehydes. In addition we have used alkaline earth hydroxides because of their ease of removal at the end of the reaction by precipitation and filtration.

The activity of the alkaline catalyst appeared to be determined to a greater degree by its pH value than by its concentration. For example, nitroethane or 1-nitropropane condensed readily with formaldehyde when catalyzed by sodium carbonate or sodium bicarbonate. 2-Nitropropane and formaldehyde condensed hardly at all in the presence of sodium bicarbonate and only very slowly with 3 per cent sodium carbonate at 30° C. On the other hand, a solution of the two reactants condenses readily when 0.1 per cent of sodium hydroxide is added. The exact action of the catalyst in this reaction is not known. It was found that pyridine, which has an ionization constant of 2.3×10^{-9}, does not catalyze the reaction of nitroethane and acetaldehyde, whereas trimethylamine ($K_i = 7.4 \times 10^{-5}$) rapidly promotes this condensation at 30-35° C. On the other hand, the condensation of 2-nitrobutane and acetaldehyde proceeds slowly in the presence of trimethylamine, and sodium hydroxide rapidly catalyzes this reaction at the temperatures employed. Nitromethane has an ionization constant of 1×10^{-11}. The rest of the nitroparaffins are considerably less acidic, carbonic acid being capable of liberating them from their salts. It is believed that the secondary nitroparaffins are considerably less acidic than the corresponding primary compounds. Judging from the yields of nitroalcohols obtained from these two types of nitroparaffins, it is indicated that the reactivity of the nitroparaffins toward aldehydes varies directly with their pH. Alkalies convert the primary and secondary nitroparaffins to their corresponding nitronic salts. The fact that several of the catalysts employed will not convert the nitroparaffins to their salts but will catalyze their condensation with aldehydes indicates that salt formation of the nitroparaffin is not essential for the condensation reaction to proceed. In fact, it has been established that the sodium salt of a nitroparaffin will not condense with an aldehyde unless the former is primary—i. e., unless there is a free hydrogen atom attached to the alpha carbon atom. It was found that when a dihydric nitroalcohol is treated with a molecular equivalent of sodium hydroxide, it is converted to the salt of a monohydric nitroalcohol containing one less carbon atom:



$$R\text{—}\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}\text{—}NO_2 + NaOH \longrightarrow R\text{—}\underset{\displaystyle CH_2OH}{C}{=}NO_2Na + HCHO + H_2O$$

On further treatment with sodium hydroxide at moderate temperatures, the monohydric alcohol does not decompose, and if the formaldehyde is removed and the sodium hydroxide neutralized, the free monohydric alcohol can be recovered. In a similar manner, nitroalcohols from secondary nitroparaffins are decomposed to the original nitroparaffin and aldehyde by sodium hydroxide. Thus it is apparent that a strong alkali will reverse the aldehyde-nitroparaffin condensation reaction and form the salt of the monohydric nitroalcohol or of the secondary nitroparaffin. Since a primary nitroparaffin is monobasic and is apparently not a stronger acid than the monohydric nitroalcohols derived from it, there is no tendency for such nitroalcohols to decompose further. This is exactly true only with nitroalcohols derived from formaldehyde, since the sodium salts of nitroalcohols derived from primary nitroparaffins and acetaldehyde were found to give cleavage products in aqueous solution. This is probably due to the fact that the aldehydes which would be liberated in case of the reversal of the condensation reaction are partially destroyed by the alkali and thus shift the equilibrium in this direction.

Previous investigators have been able to condense two molecules of a given aldehyde with the primary nitroparaffins above nitromethane only when they employed formaldehyde (*11*). However, they could apparently condense one molecule of any aldehyde and one molecule of formaldehyde with such nitroparaffins (*10*). Nitromethane has been condensed, respectively, with three molecules of formaldehyde (*5*), two molecules of aldehydes higher than formaldehyde (*14*), and two molecules of formaldehyde and one molecule of a higher aldehyde (*2*).

Early in the course of this investigation it was ascertained that nitroethane, 1-nitropropane, 1-nitrobutane, and 2-methyl-1-nitropropane will readily condense with two molecules of formaldehyde. However, in the case of acetaldehyde or butyraldehyde only one molecule of the aldehyde condenses with these nitroparaffins. Use of great excesses of the aldehydes, high concentrations of catalysts, and elevated temperatures did not suffice to cause any nitroglycols to form when using either of these two aldehydes.

When formaldehyde is condensed with any of the four mentioned primary nitroparaffins, the first molecule of the formaldehyde apparently condenses more easily than the second, but only very slightly. We thought that it might be possible to find a catalyst which would facilitate the addition of one molecule of formaldehyde to primary nitroparaffins, but would not be alkaline enough to cause the second molecule to condense to form the nitroglycol. In an attempt to form 2-nitro-1-butanol from equimolar quantities of 1-nitropropane and formaldehyde, various concentrations of sodium carbonate, sodium bicarbonate, trimethylamine, and pyridine were used as catalysts. However, in all cases considerable amounts of 2-ethyl-2-nitro-1,3-propanediol were formed, leaving a corresponding quantity of nitropropane unreacted. The use of various temperatures and times of reaction appeared to be of no avail. In order to obtain a monohydric alcohol in good yield from a primary nitroparaffin and formaldehyde, it was found necessary to use approximately a 100 per cent excess of the nitroparaffin and to use a strong base as catalyst. Any nitroglycol formed could be added to the next batch. In the presence of an alkaline material there is evidently an equilibrium between the two nitroalcohols and the primary nitroparaffin.

Conclusions

The primary and secondary nitroparaffins offer a convenient means of preparing aliphatic nitroalcohols. Owing to the presence of both the nitro and the hydroxy groups in the molecule, these compounds show promise as solvents. Their reduction to the corresponding aminoalcohols offers a means of preparing a huge number of compounds suitable for the synthesis of wetting agents, emulsifiers, and detergents. A large number of esters, ethers, and other organic chemicals can be prepared from these nitroalcohols. It is probable that some of these compounds will find their place as valuable articles of commerce.

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