

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Utilization of Aliphatic Nitro Compounds. III. Nitroalcohols Prepared from Aldehydes Containing No Other Functional Groups

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Since the development of vapor phase nitration has made the nitroparaffins readily available, and a systematic study of their condensations with aliphatic aldehydes has been published,² the use of this method for the preparation of nitroalcohols has now been studied. Three different procedures have been developed to ensure adequate yields.

In the first, the minimum amount of alkali is used as a catalyst to give a reasonable velocity and still not result in a large amount of dehydration and polymerization. In this procedure a long reaction period is normally required and the yield decreases as the complexity of the aldehyde or nitroparaffin increases. It is illustrated by the preparation of 2-nitro-3-decanol.

2-Nitro-3-decanol.—A solution of 9.4 g. (0.125 mole) of nitroethane, 25 ml. of methanol, and 0.5 ml. of 10 *N* sodium hydroxide in a 500-ml. three-necked flask was vigorously agitated while 16 g. (0.125 mole) of *n*-octanal was added, at 30–35°, and the product allowed to stand at this temperature for four days. An equivalent amount of hydrochloric acid was then added, the aqueous layer separated along with any inorganic salt, and the mixture fractionated. The methanol, traces of water, and unreacted materials were removed at room temperature by stripping under reduced pressure. The nitroalcohol was then distilled to give a light yellow liquid; b. p. 122° (1.8 mm.); yield 71.5%.

By the second procedure one mole of sodium hydroxide in concentrated solution is added, forming a stable complex which is then hydrolyzed to the nitroalcohol.^{3,4} There are no apparent side reactions if the temperature is kept below 10°. This procedure gives 85–90% yields with nitromethane and straight-chain aldehydes, but gives poor yields with other primary nitroparaffins and is not effective at all with secondary nitroparaffins. It is illustrated by the preparation of 1-nitro-2-octanol.

1-Nitro-2-octanol.—A solution of 61 g. (1.0 mole) of nitromethane and 114.1 g. (1.0 mole) of *n*-heptanal in an

(1) Abstracted from a thesis presented to the Faculty of the Graduate School of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in June, 1941. Presented before the Division of Organic Chemistry at Atlantic City, September, 1941.

(2) Hass, Hodge and Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936); Hass and Vanderbilt, *ibid.*, **32**, 34–38 (1940).

(3) Worrall, *Org. Syn.*, **IX**, 66–68 (1929).

(4) Holleman, *Rec. trav. chim.*, **23**, 298 (1904); *J. Chem. Soc.*, **88**, 58 (1905).

equal volume of alcohol was cooled to below 10°, the alcohol serving to prevent the mixture from solidifying during the addition of caustic. One mole of sodium hydroxide as a 10 *N* aqueous solution was added very slowly with good agitation, at a temperature not exceeding 10°. The alkaline mixture was diluted with ice water and hydrolyzed by the addition of the calculated amount of dilute acetic acid. The product is purified by fractionation; b. p. 120° (2 mm.); yield 88%.

The third procedure is to mix while still warm a solution of the sodium bisulfite addition product of the aldehyde and a solution of the sodium salt of the nitroparaffin.⁵ There are no undesirable by-products. Yields are about 40% with 2-nitrobutane and from 70–80% with the primary nitroparaffins. It is illustrated by the preparation of 3-methyl-3-nitro-4-hendecanol.

3-Methyl-3-nitro-4-hendecanol.—One hundred and three and one-tenth grams (1.0 mole) of 2-nitrobutane was dissolved in a solution of 12 g. of sodium hydroxide in 200 g. of water and 112.1 g. of *n*-octanal (1.0 mole) was added to a solution of 104 g. of sodium bisulfite in 500 g. of water. The two solutions were mixed while warm and the mixture, after standing for several hours in a warm place, was heated on the steam-bath until the product separated as an oil. The oil was purified by fractionation; b. p. 111° (1.5 mm.); yield 40%.

The physical constants of the nitroalcohols are shown in Table I.

Starting Materials.—The nitroparaffins with the exception of the mixed nitropentanes, were furnished by The Commercial Solvents Corporation. The nitropentanes used for the preparation of 3-methyl-3-nitro-2-hexanol were obtained by the distillation of crude nitrated pentane prepared in this Laboratory.⁶ It was used as a mixture, as the boiling points of 2-nitropentane, 3-nitropentane, and 1-nitrobutane are so close together that the compounds cannot be separated readily by fractionation. The *n*-hexanal was prepared according to "Organic Syntheses,"⁷ and the other aldehydes were commercial products.

Summary

1. Twenty nitroalcohols have been prepared by the condensation of nitroparaffins with aldehydes, (a) by the use of a trace of sodium hydroxide as a catalyst and a reaction period of four days, (b) by the addition of a molar equivalent of 10 *N* sodium hydroxide to a cold alcoholic solution of

(5) Kamlet, Brooklyn, N. Y., U. S. Patent 2,151,517 (March 21, 1939).

(6) Hass and Patterson, *Ind. Eng. Chem.*, **30**, 67 (1938).

(7) Gilman, "Org. Syn.," Coll. Vol. I, 1932, p. 253.

TABLE I
 PHYSICAL CONSTANTS OF THE NITROALCOHOLS

Name of compound	B. p., °C., and pressure	Mm.	Sp. gr., d_{25}^{25}	Refr. ind., n_D^{20}	Formula	% Nitrogen	
						Calcd.	Found ^b
3-Methyl-3-nitro-2-hexanol	97	5	1.0512	1.4522	C ₇ H ₁₅ O ₃ N	52.17 ^{a,c}	50.47
3-Methyl-3-nitro-4-nonanol	99-101	1.5	0.9835	1.4540	C ₁₀ H ₂₁ O ₃ N	59.11 ^a	58.73
3-Methyl-3-nitro-4-octanol	90-94	2.5	.9734	1.4568	C ₉ H ₁₉ O ₃ N	57.14 ^a	56.92
1-Nitro-2-octanol ^d	120	2	...	1.4500	C ₈ H ₁₇ O ₃ N	8.00	7.81
2-Nitro-3-nonanol	110	1.5	.9937	1.4508	C ₉ H ₁₉ O ₃ N	7.42	6.93
2-Methyl-2-nitro-3-nonanol	109	1	.9854	1.4525	C ₁₀ H ₂₁ O ₃ N	6.90	6.82
4-Nitro-5-hendecanol	135	2	.9550	1.4550	C ₁₁ H ₂₃ O ₃ N	6.47	6.40
3-Methyl-3-nitro-4-decanol	128	1.3	.9477	1.4578	C ₁₁ H ₂₃ O ₃ N	60.83 ^a	60.67
1-Nitro-2-nonanol	120-121	1	.9838	1.4508	C ₉ H ₁₉ O ₃ N	7.42	7.33
2-Nitro-3-decanol	125	2	.9761	1.4506	C ₁₀ H ₂₁ O ₃ N	6.90	6.61
3-Nitro-4-hendecanol	128	2	.9636	1.4509	C ₁₁ H ₂₃ O ₃ N	6.47	6.29
2-Methyl-2-nitro-3-decanol	124-125	1.2	.9784	1.4533	C ₁₁ H ₂₃ O ₃ N	6.47	6.30
4-Nitro-5-dodecanol	130	1.2	.9666	1.4522	C ₁₂ H ₂₅ O ₃ N	6.06	5.73
3-Methyl-3-nitro-4-hendecanol	111	1.5	.9521	1.4569	C ₁₂ H ₂₅ O ₃ N	62.28 ^a	62.44
2-Nitro-3-hendecanol	128	1.8	.9640	1.4513	C ₁₁ H ₂₃ O ₃ N	6.47	6.20
3-Nitro-4-dodecanol	138-140	2.2	.9622	1.4517	C ₁₂ H ₂₅ O ₃ N	6.06	5.97
2-Methyl-2-nitro-3-hendecanol	125	3	.9240	1.4524	C ₁₂ H ₂₅ O ₃ N	6.06	5.83
1-Nitro-2-hendecanol	140	2	.9587	1.4548	C ₁₁ H ₂₃ O ₃ N	6.47	6.23
2-Nitro-3-tridecanol	153-155	2	.9496	1.4618	C ₁₃ H ₂₇ O ₃ N	5.72	5.30
3-Nitro-4-tetradecanol	150-155	1.5	.9480	1.4638	C ₁₄ H ₂₉ O ₃ N	5.41	5.02

^a % Carbon (not nitrogen), by "Wet Method," Pollard and Forsee, *Ind. Eng. Chem., Anal. Ed.*, **7**, 77 (1935). ^b "Kjeldahl," Harte, *ibid.*, **7**, 432 (1935). ^c Low carbon analysis is due to the presence of 1-nitrobutane in the nitropentanes. ^d Not a new compound (2).

the nitroparaffin and aldehyde followed by dilution and hydrolysis with dilute acetic acid, and (c) by the mixing of a dilute solution of the sodium salt of the nitroparaffin with an aqueous suspension of the sodium bisulfite addition product of

the aldehyde and subsequent heating of the mixture.

2. Some of the physical constants of these nitroalcohols have been measured.

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Arsine Oxides of Naphthalene and Biphenyl¹

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Arsine oxides, derived from naphthalene and biphenyl, have been prepared by us in order that their treponemicidal activity might be investigated.

Reduction of α -naphthylarsonic acid with sulfur dioxide and potassium iodide yielded an arsine oxide identical with that obtained by Michaelis,² and by Blicke and Smith³ by other methods.

The β -naphthylarsonic acid, used by Michaelis to prepare the corresponding oxide, was shown by Brown⁴ to be a mixture of α - and β -naphthyl-

arsonic acids. β -Naphthylarsonic acid, prepared by Brown's method, yielded an arsine oxide on reduction which did not melt below 360°.

Saunders, Hamilton and Sweet⁵ have described the preparation of a number of nitro-naphthylarsonic acids. We have discovered that the more convenient Scheller-Bart reaction⁶ is equally applicable for the preparation of these compounds. Some of these nitronaphthylarsonic acids were reduced catalytically to the corresponding amino compounds by the use of Raney nickel. The yields were comparable to those ob-

(1) Paper V in the series entitled "The Preparation of Phenyl-arsenoxides."

(2) Michaelis, *Ann.*, **320**, 271 (1902).

(3) Blicke and Smith, *THIS JOURNAL*, **51**, 3479 (1929).

(4) Brown, *Trans. Kansas Acad. Sci.*, **42**, 209 (1939).

(5) (a) Saunders and Hamilton, *THIS JOURNAL*, **54**, 636 (1932); (b) Sweet and Hamilton, *ibid.*, **56**, 2408 (1934).

(6) Scheller, French Patent 624,028, *Chem. Zentr.*, **98**, II, 229 (1927); Doak, *THIS JOURNAL*, **62**, 167 (1940).