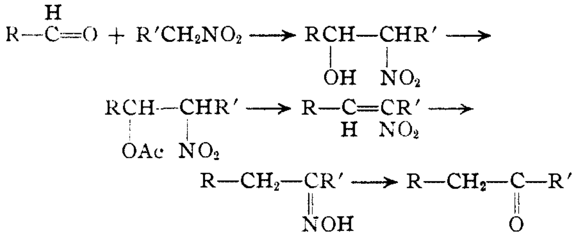
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MISSOURI]

The Preparation of Ketones from Nitroölefins

BY DOROTHY NIGHTINGALE AND J. R. JANES[1]

The purpose of the investigation was to develop a method of preparation of aliphatic ketones from nitroparaffins by the following series of reactions



$$R\text{—}\overset{H}{C}=O + R'CH_2NO_2 \longrightarrow R\underset{OH}{\underset{|}{CH}}\text{—}\underset{NO_2}{\underset{|}{CHR'}} \longrightarrow$$

$$R\underset{OAc}{\underset{|}{CH}}\text{—}\underset{NO_2}{\underset{|}{CHR'}} \longrightarrow R\text{—}\underset{H}{C}=\underset{NO_2}{CR'} \longrightarrow$$

$$R\text{—}CH_2\text{—}\underset{NOH}{\underset{\|}{CR'}} \longrightarrow R\text{—}CH_2\text{—}\underset{O}{\underset{\|}{C}}\text{—}R'$$

where R and R′ are aliphatic. It was first necessary to develop a satisfactory method for the preparation of nitroölefins.

The method of Schmidt and Rutz[2] as modified by Hass and co-workers[3,4] has been found suitable for the preparation of nitroölefins. We found that it improved the yield to add methanol to the aqueous sodium bicarbonate solution. The procedure is generally reliable and yields of nitroolefin are usually 90–95% with the best yields from esters of nitroalcohols with nine or more carbon atoms. The yield from nitroalcohol to nitroölefin via the ester is usually around 80–84%

Bouveault and Wahl[5] have shown that nitroolefins of the structure $R\text{—}\overset{H}{C}=\overset{H}{C}\text{—}NO_2$ could be reduced to the aldoxime with zinc powder and acetic acid. Hass and Susie[3] have reported that subsequent workers have been unable to repeat the work of Bouveault and Wahl, but we have found that the reduction of nitroölefins of the structure $R\text{—}\underset{H}{C}=\underset{NO_2}{C}\text{—}R'$ to the ketoxime proceeded smoothly with a 50–60% yield in most cases.

The ketoximes were hydrolyzed to ketones by refluxing with 4 *N* sulfuric acid and a hydroxylamine acceptor (40% formaldehyde). Yields of ketone are around 80%, with an over-all yield from the nitroölefin of 40–48%. Syntheses of

TABLE I

NITROALCOHOLS

Nitroalcohol	n^{25}_D	d^{25}_{25}	B. p. °C.	B. p. Mm.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1-Nitro-2-butanol	1.4425	1.1303	75	2	40.34	7.56	40.35	7.29
3-Nitro-2-butanol	1.4405	1.1264	78	17			40.34	7.65
1-Nitro-2-pentanol	1.4439	1.0810	85	2	45.11	8.27	44.83	8.52
2-Nitro-3-pentanol	1.4428	1.0915	79	2			44.99	8.51
3-Nitro-2-pentanol	1.4410	1.0839	78	2			45.23	8.05
3-Nitro-3-Me-2-butanol	1.4457	1.1042	64	2			45.32	8.53
1-Nitro-3-Me-2-butanol	1.4455	1.0900	66	1			44.83	8.15
1-Nitro-2-hexanol	1.4458	1.0564	80	1	48.98	8.84	48.65	8.93
2-Nitro-3-hexanol	1.4450	1.0547	82	2			48.66	8.83
3-Nitro-4-hexanol	1.4441	1.0603	89	2			48.75	8.75
2-Nitro-4-Me-3-pentanol	1.4473	1.0682	89	2			49.15	8.81
2-Nitro-2-Me-3-pentanol	1.4478	1.0803	75	4			49.23	8.98
1-Nitro-2-heptanol	1.4452	1.0237	105	2	52.17	9.32	52.33	9.27
2-Nitro-3-heptanol	1.4469	1.0362	92	2			52.00	9.56
3-Nitro-4-heptanol	1.4448	1.0273	92	2			52.24	9.56
1-Nitro-3-Et-2-pentanol	1.4520	1.0422	93	2	52.17	9.32	51.99	9.50
3-Nitro-5-Me-4-hexanol	1.4466	1.0405	78	2			52.30	9.56
2-Nitro-2-Me-3-hexanol	1.4488	1.0398	81	2			52.06	9.56
2-Nitro-3-octanol	1.4498	1.0227	85	2	54.86	9.72	55.01	9.71
3-Nitro-4-octanol	1.4467	1.0113	94	2			54.99	9.93
2-Nitro-4-Et-3-hexanol	1.4580	1.0277	92	2			54.93	9.94
3-Nitro-4-nonanol	1.4500	1.0087	108	2	57.10	10.05	56.85	9.74
3-Nitro-5-Et-4-heptanol	1.4516	1.0058	87	2			57.29	10.24
1-Nitro-3-Et-2-heptanol	1.4539	1.0068	110	2			57.01	10.12
3-Nitro-4-decanol	1.4470	0.9757	108	2	59.11	10.34	59.14	10.64
2-Nitro-4-Et-3-octanol	1.4542	.9965	102	2			58.81	10.53
3-Nitro-5-Et-4-nonanol	1.4530	.9831	100	2	60.83	10.60	60.59	10.82

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(1) Abstract of a portion of the dissertation by John Robert Janes in partial fulfillment of the requirements for the degree of Doctor of Philosophy, September, 1943. Present address, Hercules Powder Company, Wilmington, Delaware.

(2) Schmidt and Rutz, *Ber.*, **61**, 472 (1928).

(3) Hass and Riley, *Chem. Rev.*, **32**, 411 (1943).

(4) Hass, Hodge and Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936); **32**, 34 (1940).

(5) Bouveault and Wahl, *Bull. soc. chim.*, [3] **29**, 517 (1903).

some of these branched chain ketones such as 4-ethyl-2-octanone and 5-ethyl-3-nonanone by any other method would be long and tedious.

All efforts to condense nitroölefins such as 2-nitro-4-ethyl-2-hexene, 2-nitro-4-ethyl-2-pentene, 3-nitro-3-hexene and 1-nitro-1-heptene with butadiene and with cyclopentadiene under a variety of experimental conditions were negative, even using the experimental conditions of Alder, Rickert and Windemuth.[6]

Experimental

The nitroölefins are greenish-yellow liquids when freshly prepared and pure. The 1-nitro-1-ene olefins are unstable and gradually decompose, the 2-nitro-2-enes are somewhat more stable and the 3-nitro-3-enes are quite stable. Branched chain nitroölefins except 1-nitro-1-enes are very stable. The lower members of the series up to the nitroheptenes have sharp biting odors and are strong lachrymators, while the higher members beginning with the nitrononenes have a pleasant odor somewhat similar to camphor.

If the nitroölefins are distilled under pressures at or near atmospheric pressure, they decompose rapidly and exothermically to form a tar, sometimes with explosive violence. Distillation near 1 mm. is desirable.

TABLE II

α-NAPHTHYLURETHANS OF THE NITROALCOHOLS

Nitroalcohol	M. p., °C.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
1-Nitro-2-butanol	118–119	62.50	5.60	62.38	5.61
3-Nitro-2-butanol	122–123			62.40	5.77
1-Nitro-2-pentanol	99–100	63.57	5.97	63.32	6.23
2-Nitro-3-pentanol	126			63.62	6.21
3-Nitro-2-pentanol	100–101			63.51	5.97
3-Nitro-3-methyl-2-butanol	137			63.59	6.09
1-Nitro-3-methyl-2-butanol	97.5–98			63.66	6.05
1-Nitro-2-hexanol	103	64.56	6.34	64.39	6.64
2-Nitro-3-hexanol	136–137			64.55	6.49
3-Nitro-4-hexanol	113–114			64.50	6.27
2-Nitro-4-methyl-3-pentanol	112–113			64.50	6.38
2-Nitro-2-methyl-3-pentanol	97–98			64.30	6.37

TABLE III

ALIPHATIC NITROÖLEFINS

Compound	n^{25}_D	d^{25}	B. p., °C. (1 mm.)	Calcd., % C	Calcd., % H	Found, % C	Found, % H
2-Nitro-2-hexene	1.4513	0.9883	53	55.81	8.53	55.67	8.65
3-Nitro-3-hexene	1.4521	.9785	53			55.52	8.69
2-Nitro-4-methyl-2-pentene	1.4520	.9780	57			55.48	8.91
1-Nitro-1-heptene	1.4524	.9743	57	58.04	9.09	57.86	9.07
3-Nitro-5-methyl-3-hexene	1.4528	.9741	53			58.18	9.29
2-Nitro-4-ethyl-2-hexene	1.4602	.9551	84	61.16	9.55	61.13	9.81
3-Nitro-5-ethyl-3-heptene	1.4598	.9427	65	63.16	9.94	62.99	10.06
3-Nitro-3-decene	1.4540	.9235	97	64.84	10.27	64.57	10.41
3-Nitro-4-ethyl-2-octene	1.4616	.9343	84			64.81	10.56
3-Nitro-5-ethyl-3-nonene	1.4616	.9273	94	66.30	10.55	66.24	10.73

Preparation of Nitroalcohols and their Derivatives.—The nitroalcohols were prepared by the method of Sprang and Degering.[7] Yields were consistently 70–80%. The properties of the nitroalcohols and the solid α-naphthylurethans, not previously reported in the literature, are summarized in Tables I and II. The urethans were prepared by warming 2 cc. of the nitroalcohol and 1.5 cc. of α-naphthyl isocyanate on a water-bath until the mixture became solid. The urethans were extracted with petroleum ether (86–100°). The higher molecular weight nitroalcohols gave uncrystallizable oils. The melting points were determined in a capillary tube heated in a copper block at one degree rise per minute. The urethans precipitate from petroleum ether as fine needles or small leaflets.

The esters of the nitroalcohols were prepared by the method of Tindall.[8] The acetic anhydride was removed in a partial vacuum and the esters distilled at 1 mm. Some nitroölefin was formed during distillation. The esters were used without further purification.

Preparation of Nitroölefins.—The preparation of 3-nitro-5-ethyl-3-nonene is typical. 3-Nitro-5-ethyl-4-nonanol acetate (83 g.) was placed in a one-liter round-bottom flask with 100 cc. of a 0.5 *N* solution of sodium bicarbonate and 200 cc. of methanol and refluxed eight hours. The mixture formed a fine emulsion at reflux temperature and, as cleavage proceeded, the nitroölefin gradually separated out as the emulsion disappeared and the water layer became clear. The nitroölefin formed a thick greenish globule which came to the top of the reaction mixture on cooling. With nitroölefins below the nitroöctenes the globule settled to the bottom of the flask.

The nitroölefin was extracted with two 100-cc. portions of ether. The ether extract was washed, and dried over anhydrous sodium carbonate and distilled; b. p. 94° (1 mm.); yield, 58 g. (90%). The lower nitroölefins were distilled through a three-foot column packed with glass helices and fitted with a still-head with a total condensation and variable take-off. Yields were usually 90–95%. The higher nitroölefins were pure enough to use without fractionation. The physical properties of the nitroölefins are given in Table III. The molecular refractivities showed exaltation.

The use of solid dehydrating agents led to more or less tar formation.

Ozonolysis of 3-nitro-3-hexene followed by reductive cleavage of the ozonide yielded propionaldehyde which was identified by conversion to propional dimethone, m. p. and mixed m. p. 149–150°.

Preparation of Oximes: 5-Ethyl-3-nonanone Oxime.—Zinc dust (50 g.) was placed in a 500-cc. three-necked conical flask equipped with a motor stirrer, dropping funnel and reflux condenser. An ether solution (200 cc.) of the above nitroölefin (43 g.) was added and stirred vigorously while a solution of 25% acetic acid (110 g.) was added through the dropping funnel over a two-hour period (four hours in some cases) at such a rate that the ether refluxed gently. After all the acid had been added, the reaction mixture was heated gently until it became colorless and bubbles of hydrogen ceased to form, usually four to six hours. The zinc acetate was separated by filtration and

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(6) Alder, Rickert and Windemuth, *Ber.*, **71**, 2451 (1938).

(7) Sprang and Degering, THIS JOURNAL, **64**, 1063 (1942).

(8) Tindall, *Ind. Eng. Chem.*, **33**, 65 (1941).

TABLE IV

KETOXIMES

Oxime of	$n^{25}D$	B. p. °C.	B. p. Mm.	Calcd., % C	Calcd., % H	Found, % C	Found, % H
5-Ethyl-3-heptanone	1.4547	75–79	1	68.79	12.10	68.48	12.26
3-Decanone	1.4532	81	1	70.18	12.28	69.94	12.46
5-Ethyl-3-nonanone	1.4560	89–92	1	71.35	12.43	71.05	12.47
4-Ethyl-2-hexanone	1.4522	69	1	67.18	11.89	67.13	12.06
5-Methyl-3-hexanone	1.4428	55	1	65.12	11.63	65.32	11.89
3-Heptanone[a]	1.4522	56	1	65.12	11.63	65.45	11.87
3-Nonanone	1.4552	70	1	68.79	12.10	69.14	12.38
4-Ethyl-2-octanone	1.4534	81	1	70.18	12.28	70.31	12.41

[a] Timmermans, *Bull. soc. chim. Belg.*, **36**, 502 (1927).

extracted with ether in a Soxhlet extractor to recover absorbed oxime. The ether extract was added to the filtrate and the ether removed on a water-bath. The acetic acid was removed in a low vacuum and the residue, a greenish oil, distilled at 89–92° (1 mm.); yield 21 g. (52%). The yields of oxime were consistently 50–60%. They are viscous, strong-smelling liquids. Their properties are given in Table IV.

Preparation of Ketones: 5-Ethyl-3-nonanone.—The above oxime (17.5 g.) was refluxed one-half hour with 50 cc. of 4 *N* sulfuric acid and 22 cc. of formalin solution. The ketone was extracted with two 50-cc. portions of ether and the ether solution dried over anhydrous copper sulfate or Drierite. The ether was removed on a water-bath and the ketone distilled; b. p. 53° (1 mm.); yield 12 g. (80%).

Anal. Calcd. for $C_{11}H_{22}O$: C, 76.92; H, 12.82. Found: C, 76.62; H, 12.97.

This ketone, not described in the literature, was the only one of the ketones which would not form a solid derivative. The melting points of the semicarbazones of the other ketones agreed with those reported in the literature.

The reduction of 35 g. of 2-nitro-4-ethyl-3-hexene with hydrogen and Raney nickel at 45 lb. yielded 10 g. of 4-ethyl-2-hexanone as the principal product. A large amount of tar remained in the distilling flask.

Summary

A variety of aliphatic nitroölefins have been prepared in good yield by refluxing the acetates of nitroalcohols with an aqueous methanol solution of sodium bicarbonate.

Nitroölefins of suitable structure were reduced to the corresponding ketoximes in 50–60% yield by means of zinc and acetic acid.

The ketoximes were converted to ketones by hydrolysis with dilute sulfuric acid in the presence of formalin.

The α-naphthyl urethans of a number of nitroalcohols have been described.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

The Reaction of Citronellal with Benzylmagnesium Chloride[1]

BY WILLIAM G. YOUNG AND SAMUEL SIEGEL

In attempting to prepare α-benzylcitronellol by the addition of citronellal to benzylmagnesium chloride, Rupe[1a] isolated an almost colorless, viscous liquid, distilling at 243–244°(9 mm.). After determining the elementary analysis for carbon and hydrogen, and the value of the molecular weight of the substance in benzene, he suggested that this material was formed by the addition of two moles of benzylmagnesium chloride to one mole of citronellal, the second mole of the Grignard reagent adding to the ethylenic double bond of the aldehyde. Later Gilman and Schulz[2] sought to disprove this contention by an indirect method. They added the aldehyde to a large excess of benzylmagnesium chloride. The mixture was then treated with carbon dioxide and the resulting acids were isolated. Since the product of the addition of a Grignard reagent to an ethylenic double bond would contain a carbon to magnesium linkage, it should react with carbon dioxide to form the salt of a carboxylic acid. Gilman and Schulz isolated phenylacetic acid but found no indication of the presence of any other acid. They concluded that the Grignard reagent had not added to the ethylenic double bond. Although these workers also isolated a liquid having the same properties as that reported by Rupe, they did not further investigate it. Since this indirect proof is not conclusive[3,4] and because certain evidence obtained in this Laboratory pointed to the possibility of the addition of Grignard reagents to the ethylenic double bond, a more thorough investigation of the above reaction was carried out.

Although Rupe was unable to obtain better than a 25% yield of α-benzylcitronellol, we have

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[1] Presented before the Division of Organic Chemistry at the Pittsburgh meeting of the American Chemical Society, Sept., 1943.

[1a] Rupe, *Ann.*, **402**, 161 (1913).

[2] H. Gilman and W. F. Schulz, THIS JOURNAL, **52**, 3588–3590 (1930).

[3] Kharasch, *Ann. Survey of Am. Chem.*, **5**, 193 (1930).

[4] Gilman and Schulz, THIS JOURNAL, **53**, 2799–2801 (1931).