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The Synthesis of Tertiary Nitroparaffins^{1,2}

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Permanganate oxidation of *t*-carbinamines, RR'R''C-NH₂, to RR'R''C-NO₂ (70–80% yields) provides the first practical synthesis of *t*-nitro compounds.

While tertiary nitroparaffins have been known for many years, they have in no case been obtained by reactions which could be regarded as synthetically useful. Thus, liquid phase nitration generally involves heating small amounts of a hydrocarbon in sealed tubes with dilute nitric acid to 130–150° for prolonged periods. A large number of tubes are required and they need to be opened for "periodic relief of pressure"; complex mixtures are produced and the yields of pure *t*-nitrocompounds are poor.³

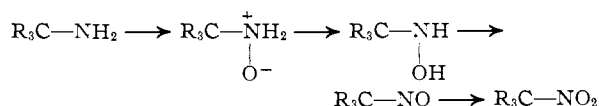
The vapor phase nitration process devised by Hass, Hodge and Vanderbilt,⁴ despite its great commercial importance, can hardly be regarded as a laboratory synthesis, the more so since it gives rise to complex mixtures. And, finally, recent work has demonstrated that the classical reaction of silver nitrite with alkyl halides is worthless for the preparation of tertiary nitroparaffins.⁵

The present paper describes a simple and reliable procedure for oxidizing *t*-carbinamines, RR'R''C-NH₂, to the corresponding *t*-nitro compounds using potassium permanganate at 25–30°. The procedure has the virtue of being applicable, without alteration, to a wide variety of amines and, as shown in Table I, excellent yields of pure *t*-nitro compounds are obtained. This new method also has the advantage of starting with *t*-carbinamines, substances which have now become easily accessible.⁶

In these permanganate oxidations the solvent employed is of considerable importance. Although oxidation of *t*-butylamine in aqueous solution gave an 83% yield of *t*-nitrobutane, the oxidation of higher molecular weight amines proved to be more of a problem because of their insolubility in water. The use of elevated temperatures and protracted reaction times failed to produce the desired nitro compounds in significant yields under heterogeneous conditions. Addition of acetic acid to the reaction mixture solubilized the amines, but the yields of nitro compounds remained low (30–60%) and very variable; also, a considerable portion of the amine failed to react. Efforts to improve things by vary-

ing the mole per cent. of acetic acid were unsuccessful.

In contrast, the desired oxidation proceeded smoothly and in excellent yields when a mixture of 80% acetone and 20% water was used, especially when the pH was controlled by adding magnesium sulfate (Table I). Although no effort was made to study the mechanism of these oxidations it seems reasonable to assume that the following sequence is involved



That nitroso compounds are intermediates seems clear from the characteristic blue color which the product possesses when oxidation is incomplete.

In only one instance did the permanganate oxidation fail to give the desired *t*-nitro compound. When oxidation of triphenylmethylamine to triphenylnitromethane was attempted the only product isolated, aside from a 40% recovery of the amine, was triphenylcarbinol (33% yield based on the amine which had reacted).

The use of alkaline hydrogen peroxide was briefly examined. Oxidation of *t*-butylamine gave *t*-nitrobutane in 31% yield. Since, for laboratory work, hydrogen peroxide offers no advantage, its use in these oxidations was not investigated further.

Acknowledgment.—We thank the Rohm and Haas Co. and the Continental Oil Co. for generous gifts of *t*-carbinamines. Our best thanks are also due to the Standard Oil Co. of Indiana for a very substantial gift of 1-methylcyclopentene.

Experimental⁷

With the exception of *t*-nitrobutane, the yields reported in Table I were obtained using the following procedure for the preparation of 2-nitro-2,4,4-trimethylpentane.

Preparation of 2-Nitro-2,4,4-Trimethylpentane.—Twenty-five and eight-tenths grams (0.2 mole) of 2-amino-2,4,4-trimethylpentane (*t*-octylamine) is dissolved in 500 ml. of acetone and then 125 ml. of water is added. To the well stirred solution, 30 g. of magnesium sulfate (J. T. Baker purified, dried powder),⁸ was added in one portion and then 190 g. (1.12 moles) of potassium permanganate was added, in portions, over the course of one hour.⁹ After addition of the

(7) Analyses are by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and by Dr. C. S. Yeh and Mrs. S. L. Margerum, Purdue University.

(8) This product, we are informed by the J. T. Baker Co., has ca. 70% MgSO₄ the remainder being water. Presumably, a proportionally larger amount of MgSO₄·7H₂O will work as well but this point was not tested.

(9) Care should be taken that the permanganate does not cake up on the bottom of the flask. In one run when this happened local overheating occurred and the reaction of acetone with permanganate consumed a large part of the oxidizing agent.

(1) Paper XV in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds." A preliminary account of this work appeared in THIS JOURNAL, **76**, 4494 (1954).

(2) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF 18(600)310.

(3) See, e.g., S. S. Nametkin and K. S. Zabrodina, *Doklady Akad. Nauk. S.S.S.R.*, **75**, 395 (1950); *C. A.*, **45**, 6998 (1951).

(4) H. B. Hass, E. B. Hodge and B. M. Vanderbilt, *Ind. Eng. Chem.*, **28**, 339 (1936).

(5) N. Kornblum, R. A. Smiley, H. E. Ungnade, A. M. White, B. Taub and S. A. Herbert, THIS JOURNAL, **77**, 5528 (1955).

(6) J. J. Ritter and J. Kalish, *ibid.*, **70**, 4048 (1948).

TABLE I
 SYNTHESIS OF *t*-NITRO COMPOUNDS

Compound	Yield, %	B.p.,		n_D^{20}	Carbon, %		Hydrogen, %		Nitrogen, %	
		°C.	Mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>t</i> -Nitrobutane ^a	83	127-128	760	1.3980 ^{b,c}	46.59	46.46	8.80	8.74	13.78	13.55
2-Nitro-2,3-dimethylbutane	71	173-174	760	^d					10.68	10.58
2-Nitro-2,4-dimethylpentane	82	60	8	1.4243					9.65	9.88
2-Nitro-2,4,4-trimethylpentane	77	54	3	1.4314 ^{e,f}	60.34	60.33	10.76	10.77	8.80	8.78
1-Nitro-1-methylcyclopentane	72	75	20	1.4498 ^g	55.80	56.06	8.58	8.79	10.84	10.63
1-Nitro-1-methylcyclohexane	73	80	10	1.4582 ^h	58.77	58.66	9.08	9.20	9.78	9.83
1-Nitro-1,4-dimethylcyclohexane	70	79.5-81	5	1.4548					8.91	9.32
1,8-Dinitro- <i>p</i> -menthane	61 ⁱ				52.16	52.43	7.88	7.85	12.13	11.92

^a This oxidation carried out in water; all others in 80% acetone-20% water. ^b At 28°. ^c M.p. 25-26°. ^d M.p. 29-29.5°. ^e At 28°; ref. 3 reports n_D^{20} 1.4360. ^f M.p. 23.5-23.7°. ^g Nametkin (*Chem. Zentr.*, **83**, I, 1702 (1912)) reports b.p. 86-88° (30 mm.), n_D^{20} 1.4493. ^h Nametkin (*Chem. Zentr.*, **81**, II, 1377 (1910)) gives n_D^{20} 1.4580. ⁱ M.p. 104-106°; presumably a mixture of *cis-trans* isomers. M. Konawalow (*Chem. Zentr.*, **72**, II, 343 (1906)) gives m.p. 107.5-108.5°.

permanganate, stirring is continued at 25-30° for 48 hours. The stirred mixture is then subjected to the vacuum of a water-pump while being maintained close to 25-30° by external warming. When stirring becomes difficult distillation is discontinued, ca. 100-200 cc. of water is added, and the mixture is steam distilled. The pale blue distillate is taken up in petroleum ether¹⁰ (35-37°) and dried over magnesium sulfate. Rectification through a small column packed with glass helices gave 24.3 g. (77% yield) of colorless nitro compound. There was no forerun and the amount of residue was insignificant. All fractions had b.p. 54° (3 mm.) and n_D^{20} 1.4314.

Preparation of 1,8-Dinitro-*p*-menthane.—Here, at the end of the 48-hour reaction period, 200 ml. of benzene was added and the mixture cooled to 5°. The excess permanganate was reduced with aqueous 15% sodium bisulfite and the manganese dioxide separated by filtration. The aqueous layer of the filtrate contained no unreacted amine and was discarded. The benzene phase was dried and passed through basic alumina. In this way 19 g. (0.1 mole) of the diamine gave 16.8 g. (61% yield) of a mixture of the *cis* and *trans* forms of the dinitro compound, a white powder of m.p. 104-106°, analytically pure (Table I).

Preparation of *t*-Nitrobutane.—*t*-Butylamine (100 g.) was added to a stirred mixture of 650 g. of potassium permanganate and 3 l. of water in the course of 15 minutes. The temperature rose to 45° and, after stirring for eight hours without external heating, the mixture was held at 55 ± 5° for another eight hours. The product was isolated by steam distillation, washed with dilute hydrochloric acid, with water and then dried. A total of 117 g. (83% yield) of *t*-nitrobutane was collected as eleven fractions (b.p. 127-128°), all of which had n_D^{20} 1.3980 and m.p. 25-26°.

Attempted Preparation of Triphenylnitromethane.—When 5.3 g. of triphenylmethylamine was treated with potassium permanganate in 80% acetone-20% water for 193 hours 40% of the amine was recovered. In addition 1.05 g. of white triphenylcarbinol, m.p. and mixed m.p. 162-162.5°, was obtained.

Amines.—Except for triphenylmethylamine, the requisite amines were either gifts or were obtained from olefins by the excellent procedure of Bortnick¹¹; cf. Table II.

(10) Extraction of this petroleum ether solution with 15% aqueous sulfuric acid showed that none of the original amine was present.

(11) N. M. Bortnick, U. S. Patent 2,623,023, March 17, 1935.

Triphenylmethylamine was prepared by bubbling ammonia gas through a solution of 25 g. of triphenylchloromethane in 150 ml. of dry benzene. After adding Celite, the ammonium chloride was removed by filtration and the

 TABLE II
t-CARBINAMINES

Compound	°C.	B.p.		n_D^{20}	Nitrogen, %	
		°C.	Mm.		Calcd.	Found
<i>t</i> -Butylamine	45	760		1.3788		
2-Amino-2,3-dimethylbutane	173-174	760		1.4126	13.85	13.99
2-Amino-2,4-dimethylpentane	52.5	68		1.4110 ^a	12.18	12.11
2-Amino-2,4,4-trimethylpentane	140	760		1.4240		
1-Amino-1-methylcyclopentane	114	760		1.4420	14.21	14.41
1-Amino-1-methylcyclohexane	53	30		1.4539 ^b	12.40	12.60
1-Amino-1,4-dimethylcyclohexane	56.5	20		1.4478 ^c	11.01	11.27
1,8-Diamino- <i>p</i> -menthane	97-99	6		1.4805		

^a Chonin [*Chem. Zentr.*, **80**, II, 587 (1909)] gives b.p. 121-122.2° (753 mm.), n_D^{20} 1.4199. ^b Markownikow [*Chem. Zentr.*, **71**, II, 630 (1900)] gives n_D^{20} 1.4547. ^c *Anal.* Calcd. for C₈H₁₇N: C, 75.5; H, 13.5. Found: C, 75.4; H, 13.7.

amine was precipitated as the hydrochloride by passing in hydrogen chloride. Treatment of the hydrochloride with 20% aqueous sodium hydroxide gave a 40% yield of the amine as white crystals, m.p. 105°, lit. m.p.¹² 103°.

WEST LAFAYETTE, INDIANA

(12) Krause and Rosen, *THIS JOURNAL*, **47**, 2744 (1925).