Convenient Oxidation of Oximes to Nitro Compounds with Sodium Perborate in Glacial Acetic Acid[1]

George A. Olah,* Pichika Ramaiah, Chang-Soo Lee, G. K. Surya Prakash*
Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California 90089-1661, USA
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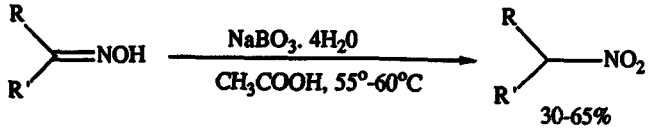
Abstract: A convenient oxidation of oximes (11 examples) to nitro compounds has been developed using sodium perborate in glacial acetic acid.

Nitroalkanes are an important class of compounds in organic chemistry.[2] They have been prepared from alkyl halides[3], primary amines[4], oximes[5] and nitroso[6] compounds. Direct nitration of alkanes was also reported[7] using stable nitronium salts as nitrating agents. Iffland developed[8] a three-step method for the oxidation of oximes into nitro compounds. Initial bromination to bromo nitroso compound, followed by oxidation with a mixture of nitric acid and 30% hydrogen peroxide, and subsequent debromination with sodium borohyride gives the nitro compound. Barnes has also reported[9] the synthesis of secondary nitroalkanes involving several steps.

Sodium perborate is an inexpensive oxidant and is used for a variety of oxidations. Oxidation of anilines, sulfides, ketones, hydroquinones, aromatic aldehydes, iodoarenes, aromatic nitriles, azines, sulphur heterocycles, benzylic alcohols, α-hydroxy carboxylic acid, 1,2-diketones, α-hydroxyketones, 1,2-diols and unsaturated compounds has been reported.[10] We have recently carried out[11] direct electrophilic hydroxylation of aromatics with sodium perborate/ triflic acid. In continuation of our studies, we report the one-step oxidation of aldoximes and ketoximes in glacial acetic acid to the corresponding primary and secondary nitro compounds under mild conditions.

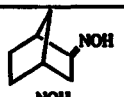
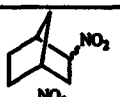
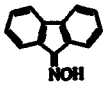
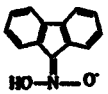
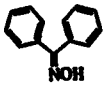
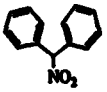
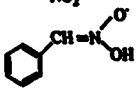
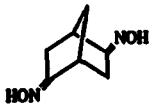
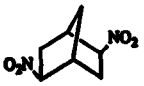


Oximes when treated with sodium perborate in glacial acetic acid at 55-60°C give the parent nitro compounds with some of the corresponding carbonyl compounds as by-products. The ratio of oxime to sodium perborate was varied from 1:1 to 1:6. With 1:1 substrate:reagent ratio, the nitro compounds were obtained only in low yield. On the other hand, oxidation with a 1:6 substrate:reagent ratio gave the nitro compound in 30 to 65% yield. In the case of heptaldehyde oxime, the corresponding nitro compound was obtained only in 28-30% isolated yield. The yield of nitro compound is dependent on the reaction conditions. For example, benzophenone oxime was recovered unchanged along with some benzophenone after 2 h at room temperature. At 55°C, a 60% yield of nitrodiphenylmethane was obtained. Under similar conditions, the oxidation of bicyclo[2.2.1]norbornanone-2-oxime gave 2-nitro-bicyclo[2.2.1]norbornane in 65% yield. 9-Fluorenone oxime and benzaldehyde *syn*-oxime gave *aci*-nitro compounds. The results are summarized in Table-1.

The presently developed method is a convenient, safe and general procedure for the preparation of primary and secondary nitro compounds. The method is also applicable to sterically hindered oximes where the use of peroxytrifluoroacetic acid[5a] generally fails. Whereas the preparation of peroxytrifluoroacetic acid involves the use of 90% hydrogen peroxide (not readily available and necessitating great care), the presently reported method uses commercially available, inexpensive and safe sodium perborate tetrahydrate and can be applied to a wide variety of oximes.

Typical procedure for the oxidation of oximes with sodium perborate tetrahydrate:
Bicyclo[2.2.1]norbornanone-2-oxime (1.0 g, 8 mmol)

Table 1. Oxidation of oximes with $NaBO_3.4H_2O$ in glacial acetic acid at 55-60°C

Oximes	Reaction time (h)	Product	Yield (%)	m.p.°C or bp°C(bath)/Torr Found	Reported	Ref.
	4		65	130/3	125/2	4f
	2		58	80/5	90/40	5a
	1		55	82/2	58/3	5a
	2		52	125/1.5	61/0.45	12
	2		42	118	116-118	13
	2		60	86	84	14
	1		45	165	165-166	15
	2		42	92	90-91	16
	4		45	157/2.5	110-115/0.6	17
	2		54	156	-	-
	1		30	120/5	74-76/4	5a

was dissolved in 50 ml of glacial acetic acid in a dry three-necked round bottomed flask. The flask was immersed in an oil bath at a temperature of 55°C. In portions, solid sodium perborate tetrahydrate (6.20 g, 40 mmol) was added with vigorous stirring over a period of 30 minutes. After the addition, the reaction mixture was stirred at the same temperature for 4 h. After cooling, the reaction mixture was treated with 4 x 25 mL ice cold saturated solution of sodium bicarbonate, followed by extraction with ether (2 x 50 mL). The organic layer was washed several times with cold water, dried over anhydrous $MgSO_4$ and evaporated. The crude product was passed through a silica gel column eluted with chloroform-pentane (1:4). The obtained product was further purified by vacuum distillation to give 2-nitrobicyclo[2.2.1]-norbornane (0.74 g) as a yellow liquid in 65% yield, b.p. 130°C(bath)/3 mm.

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References and Notes

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