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Organic Preparations and Procedures International: The New Journal for Organic Synthesis
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uopp20

DIRECT REGENERATION OF CARBONYL COMPOUNDS FORM OXIMES WITH PEG-NO_2

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Published online: 18 Feb 2009.

To cite this article: Xinming Liu , Qingzhi Zhang , Shensong Zhang & Jinming Zhang (2001) DIRECT REGENERATION OF CARBONYL COMPOUNDS FORM OXIMES WITH PEG-NO_2 , Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 33:1, 87-90, DOI: 10.1080/00304940109356578

To link to this article: http://dx.doi.org/10.1080/00304940109356578

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ORGANIC PREPARATIONS AND PROCEDURES INT., 33 (1), 87-102 (2001)

OPPI BRIEFS

DIRECT REGENERATION OF CARBONYL COMPOUNDS FORM OXIMES WITH PEG-NO_2

Submitted by (09/25/00)

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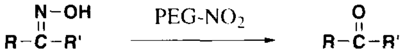
Oximes serve as efficient groups for protection and/or the separation and purification of carbonyl compounds and there has been considerable interest in the development of mild techniques for the conversion of oximes into carbonyl compounds. The classical method for the cleavage of oximes to parent aldehydes and ketones is hydrolysis under acid conditions, which is not suitable for acid sensitive compounds.[1] A number of methods for the regeneration of carbonyl compounds from corresponding oximes have been reported recently.[2-12] Although some of these have had some degree of success compared with the classical hydrolysis methods,[13-15] only a few are available to regenerate carbonyl compounds from oximes under mild conditions.[2-3] Trimethylammonium chlorochromate absorbed on alumina (TMACC/alumina)[16] and ammonium chlorochromate absorbed on alumina (ACC/alumina)[17] proved to be a mild and selective reagent for the oxidative cleavage of oximes, although aromatic aldoximes containing electron-withdrawing group gave poor yields.

Polyethylene glycol-nitrogen dioxide (PEG-NO_2, MW=300) was reported to oxidize aromatic alcohols into corresponding aldehydes or ketones.[18] The PEG-NO_2 adduct is formed by the weak attraction between the lone electron pair of oxygen and the partial positive charge on the nitrogen of NO_2, which make the oxidative power of NO_2 mild, and the structure of PEG-NO_2 is similar to that of an alkyl nitrate.[18] The PEG-NO_2 solution is best used immediately as it decomposes slowly at room temperature. However, the solution may be kept at 0° for two weeks without significant decomposition. We describe here a new mild and convenient method for the regeneration of aldehydes or ketones from the corresponding oximes in excellent yields under non-aqueous conditions using this reagent.



$$R-\overset{\overset{N-OH}{\|}}{C}-R' \xrightarrow{\text{PEG-}NO_2} R-\overset{\overset{O}{\|}}{C}-R'$$

The reaction is performed in the aprotic solvent PEG under homogeneous conditions and is easily carried out. Our experiments show that PEG-NO_2 cleaves oximes into their corresponding carbonyl compounds selectively and in excellent yields at room temperature. This method avoids the low temperature required in the N_2O_4 procedure[8] needed and overcomes the defects of other previously reported methods. GC analysis of the tail gas of the reaction showed that it only contained N_2, so the secondary pollution from NO_x is avoided. Therefore, PEG-NO_2 is a effective reagent for the selective oxidation of oximes. All the products obtained were characterised by mp, IR, ^{1}H NMR and elemental analyses as well as by comparison with authentic samples (see Table).

In summary, this new method for the regeneration of carbonyl compounds has some practical merits over previously reported methods making possible the selective oxidation of oximes under mild and non-aqueous reaction condition.

Table Oxidative Cleavage of Oximes with PEG-NO_2

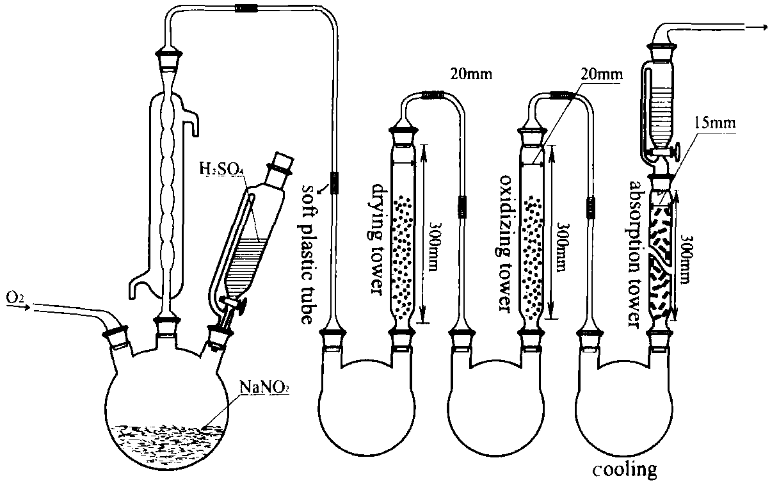
Entry	Product	Time	bp/mp °C (*lit.*)[19] of	Yield[a]
	(hours)	product	(%)	
1	Acetophenone	4.0	201.3(202)	79
2	*p*-Nitroacetophenone	4.5	79.5-80.5(80-81)	70
3	Benzophenone	4.5	48-49(48.5-49)	80
4	Cyclohexanone	3.0	154.7(155)	73
5	*3*-Pentanone	3.5	101(101.5)	62
6	Benzaldehyde	3.0	178.6(179)	78
7	*o*-Hydroxybenzaldehyde	3.0	197(196-197)	86
8	*p*-Methoxybenzaldehyde	3.0	247.4(248)	85
9	*m*-Nitrobenzaldehyde	3.5	57-58(58)	72
10	*p*-Bromobenzaldehyde	3.5	58.5-59.5(59-60)	83
11	Cinnamaldehyde	3.0	245-246(246)	84
12	Furfural	3.0	161.8(162)	58
13	Heptaldehyde	2.0	152.3(152. 8)	68

a. Yields refer to pure isolated products, characterized by comparison of their bp/mp, IR, ^{1}H NMR and elemental analyses with authentic samples.

EXPERIMENTAL SECTION

Melting points were measured on a Kofler apparatus and are uncorrected. IR spectra were obtained on a FTS-40 infrared spectrophotometer, ^{1}HNMR spectra were recorded on a Bruker DPX-400 spectrometer using TMS as an internal standard. Elemental analyses were performed by a PE-400 microelemental analyzer. The oxidizing agent employed in the oxidizing tower was prepared in the following manner: 5 g of CrO_3 was dissolved in 4 g water, and 95 g of quartz sand (20-30 mesh) was added. The mixture was stirred thoroughly and then dried at 120° to give the quartz sand carrying chromium trioxide.

General Procedure for the Preparation of PEG-NO_2 Adduct.- To 21.1 g (0.3 mol) of sodium nitrite (98%) in a three-necked round-bottomed flask was added dropwise 18 g (0.18 mol) of conc. sulfuric acid (98%) *via* a constant pressure funnel. The evolved gases were then blown by a stream of oxygen (most of the NO was converted into NO_2 at the same time) through a condenser into a drying tower (15 mm x 300 mm), packed with *ca.* 80 g of a mixture of phosphorous pentoxide and quartz sand (P_2O_5 : SiO_2 = 1:1 in wt.), then through an oxidizing tower (15 mm x 300 mm), packed with *ca.* 100 g of quartz sand carrying chromium trioxide and finally into a flask connected to an absorption tower, packed with glass rings (2 mm x 4 mm). When the gases reached the bottom of the oxidizing tower, 30 mL of PEG (MW = 300) was added dropwise through a constant pressure funnel to the absorption tower to rinse the glass ring. The NO_2 gas then entered into the absorption tower and counterface absorption was effected. Control of the rate of addition of PEG and of sulfuric acid and the flow of oxygen allows the complete absorption of NO_2 (the proper rate may be determined if the upper space of the constant pressure funnel is colorless). Once the addition of sulfuric acid was complete, the gas-producing flask was heated until the color of NO_2 was no longer evident. The oxygen was blown for a little longer to drive out any residual NO_2 completely into the absorption flask and tower. The absorption solution collected in the bottom flask (cooled to 5-10°) of the absorption tower is the PEG-NO_2 adduct, which concentration is assumed to be 10 moles / liter theoretically (see Fig.).



General Procedure for the Oxidation of Oximes.- In a typical experiment, 4 mmol of oxime was dissolved in 4 mL PEG, and 0.1 mL PEG-NO_2 (containing 1 mmol NO_2) was added at 15-25 °C with stirring. Upon completion (monitored by TLC), the reaction mixture was diluted with 15 mL of ethyl ether and washed with 12 mL water. The aqueous layer was extracted with 3 x 10 mL of ethyl ether. The combined ethereal layer was washed with water and dried over anhydrous magnesium sulfate. Removal of the solvent gave a residue which upon purification by column chromatography on silica gel using *n*-hexane:dichloromethane (1:1 v/v) as the eluent, gave the corresponding carbonyl compounds. The products obtained were identified by comparison of their bp/mp, IR, ^{1}H NMR and elemental analyses with those of authentic samples and literature references.

Acknowledgement.- This program is supported by the National Science Foundation of China and Henan Province Education Committee.

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