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A Mild Oxidant for the Regeneration of Carbonyl Compounds from Oximes in Nonaqueous Condition

Qing Zhi ZHANG*, Shen Song ZHANG, Xin Ming LIU, Jin Ming ZHANG

College of Chemistry and Environmental Science,
Henan Normal University, Xinxiang 453002

Abstract: Dioxane-NO_2 was employed to oxidize oximes to corresponding aldehydes and ketones in high yield in nonaqueous condition at room temperature. The reaction proved to be mild and selective.

Keywords: Dioxane-NO_2, oxidize, oximes, ketones, aldehydes.

Since oximes have been empolyed as ketone or aldehyde functional group equivalents in synthetic organic chemistry, the conversion of oximes into their corresponding carbonyl compounds has received considerable attention.

The classical method for the cleavage of oximes to parent aldehydes and ketones is hydrolysis in acid, which is not suitable for acid sensitive compounds[1-2]. In recent years, cleavage of oximes with ozone[3], nitrogen tetraoxide[4], copper chloride[5] and bromine[6] have been developed with some degree of success and advantage over classical hydrolysis method[7-9]. However, in these methods, some require strong oxidative conditions in aqueous media[6], some need low[4] or high[5] reaction temperature and the others have low selectivity in oxidation[3]. Therefore, there are few methods available to regenerate carbonyl compounds from corresponding oximes under mild conditions. ACC/alumina[10] proved to be a mild and selective reagent for the oxidative cleavage of oximes, but the oxidation of aromatic aldoximes containing electron-withdrawing group gave poor yields.

The NO_2 gas was absorbed on dioxane to form dioxane-NO_2 adduct. This adduct was found to be a new oxidizing agent to convert oximes into their corresponding carbonyl compounds under mild condition.

Comparing with the IR spectrum of dioxane, the IR spectrum of the dioxane-NO_2 absorbent solution indicated the new peaks at 1350 cm^{-1}, 875 cm^{-1} and 890 cm^{-1}. The 1350 cm^{-1} absorption is due to NO_2 in the absorbent solution, which shifted 30 cm^{-1} to the low-frequency side compared with that of NO_2. The 875 cm^{-1} and 890 cm^{-1} signals are due to ring-shaped skeletal vibrations of dioxane in dioxane-NO_2, which shifted correspondingly 45 cm^{-1} and 50 cm^{-1} to the high-frequency side compared with that of dioxane. This suggests that the dioxane-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. This fact makes the oxidative power of NO_2 to be mild. Therefore, Dioxane-NO_2

oxidizes oximes selectively.

The reaction was performed in aprotic solvent dioxane. It was homogeneous phase reaction. Our experiments show that dioxane-NO_2 cleaves oximes into their corresponding carbonyl compounds selectively and in excellent yields at room temperature. This method can avoid the low temperature N_2O_4 and overcome the defects of previously reported methods. All the products obtained were characterised by mp, IR, ^1H NMR and elemental analysis and finally by comparison with authentic samples (see **Table**).

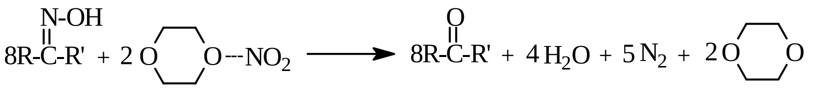
Table Oxidative cleavage of oximes with dioxane-NO_2

Entry	Substrate	Time (hours)	m.p. °C (lit.)[11] of 2,4-DNP	Yield[a] (%)
1	acetophenone oxime	4.0	236.5-237.5(237)	81
2	*p*-nitroacetophenone oxime	4.5	264-267(-[b])	70
3	benzophenone oxime	4.5	236-239(238)	82
4	cyclohexanone oxime	3.0	158.5-161(160)	75
5	3-pentanone oxime	3.5	154-156(156)	62
6	benzaldehyde oxime	3.0	235.5-237(237)	76
7	*o*-hydroxybenzaldehyde oxime	3.0	251-253(248-252)	86
8	*p*-methoxybenzaldehyde oxime	3.0	254-255(254)	85
9	*m*-nitrobenzaldehyde oxime	3.5	290.5-292(291-292)	88
10	*p*-bromobenzaldehyde oxime	3.5	259-260(260-261)	84
11	benzalacetaldehyde oxime	3.0	200-202(200.5-201.5)	85
12	furfural oxime	3.0	199.5-2(202)	63
13	heptaldehyde oxime	2.0	105.5-107(107)	70

a. Yields were based on 2,4-dinitrophenylhydrazone derivatives identified by melting points and spectra characteristics.

b. Calc. for $C_{14}H_{18}N_5O_6$: C, 48.70; H, 3.19; N, 20.29; Found: C, 48.83; H, 3.24; N, 20.41

In our method, the carbonyl compounds were obtained in highest yields from the corresponding oximes when the ratio of oxime and dioxane-NO_2 was 4. GC analysis of the tail gas of the reaction showed that NO_2 in dioxane-NO_2 adduct is reduced to N_2 and the secondary pollution of NO_x is avoided. The reaction equation is as follows:



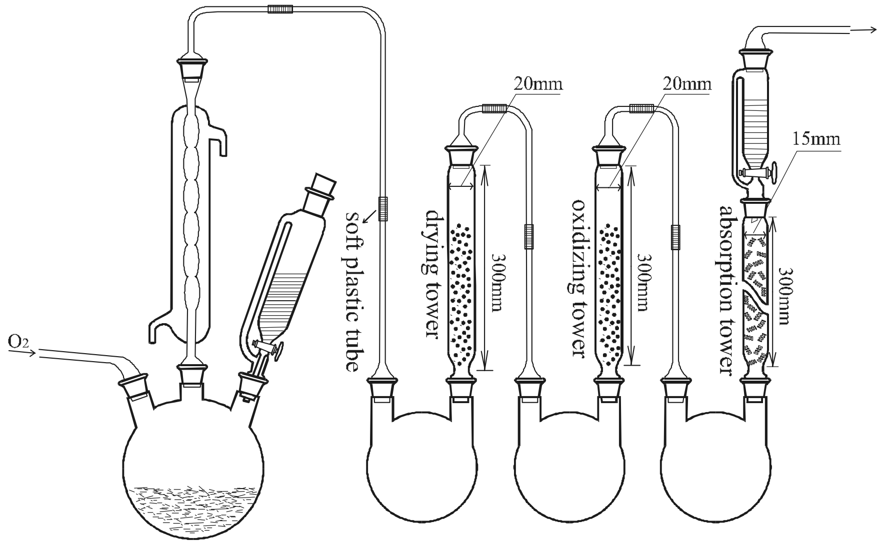
In summary, this new method for the regeneration of carbonyl compounds has some practical merits over previously reported methods. It will be able to be employed for the selective oxidation of oximes in excellent yields under mild reaction condition. Particularly, dioxane is an aprotic solvent, many substrates have a good solubility in it. It is very benefit for organic synthesis.

Experimental Section

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 then 95 g of quartz sand (20-30 mesh) was added. The mixture was stirred thoroughly and then dried at 120°C to give the quartz sand carrying chromium trioxide. Melting points were measured on a Kofler apparatus and the thermometer was uncorrected. A FTS-40 infrared spectrophotometer was utilized to record spectra of samples. ^1H NMR spectra were obtained on a Bruker DPX-400 spectrometer using TMS as an internal standard. Elemental analysis were performed on a PE-2400 microelemental analyser.

General Procedure for the Preparation of Dioxane-NO_2 Adduct

Figure Apparatus for preparation of dioxane-NO_2 Adduct



To 21.1 g (0.3 mol) of sodium nitrite (98%) in a three-neck round-bottom flask (see **Figure**) 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 (packed with *ca.* 80 g of the mixture of phosphrous pentaoxide and quartz sand, $P_2O_5 : SiO_2 = 1:1$ in wt.), then through an oxidizing tower (packed with *ca.* 100 g of quartz sand carrying chromium trioxide.) and finally into the flask connected to an absorption tower (height 300 mm, inside diameter 15 mm, packed with glass ring). When the gases reached to the bottom of the oxidizing tower, 26.5 g (0.3 mol) of dioxane was added dropwise through a funnel to the absorption tower to rinse the glass ring. The NO_2 gas then entered into the absorption tower and the counterface absorption was effected. Control of the rate of addition of dioxane 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 chase any residual NO_2 completely into the absorption flask and tower. The absorption solution collected in the bottom of flask under the absorption tower is the dioxane-NO_2 adduct.

General Procedure for the Oxidation of Oximes

4 mmol oxime was dissolved in dioxane (4ml) and dioxane-NO_2 (1mmol) was added at 15-25 ^{o}C with stirring. The reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated *in vacuo*. The product was isolated as 2,4-dinitrophenylhydrazone of corresponding carbonyl compound to fix quantity. The products obtained were identified by comparing their mp, IR, ^{1}H NMR and elemental analysis with those of authentic samples and literature references.

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