

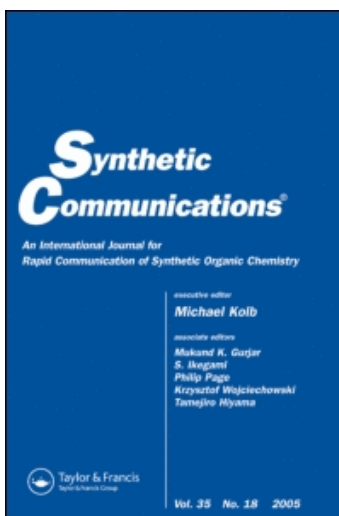
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### An Efficient and Highly Selective Method for Deoxygenation of Ketoximes

N. Chidambaram<sup>a</sup>; K. Satyanarayana<sup>a</sup>; S. Chandrasekaran<sup>a</sup>

<sup>a</sup> Department of Chemistry, Indian Institute of Technology, Kanpur, India

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**AN EFFICIENT AND HIGHLY SELECTIVE METHOD FOR  
DEOXIMATION OF KETOXIMES**

N. Chidambaram, K. Satyanarayana and S. Chandrasekaran\*

Department of Chemistry, Indian Institute of Technology,  
Kanpur 208 016, India

A combination of pyridinium dichromate/tert-butyl hydroperoxide (1:1) has been found to be an excellent reagent for the highly selective regeneration of ketones from ketoximes.

Regeneration of carbonyl compounds from its derivatives under mild conditions is an important process in synthetic organic chemistry. Many methods have been reported in the literature for the oxidative cleavage of oximes and semicarbazones,<sup>1</sup> N,N-di-methyl hydrazones<sup>2</sup> and 2,4-dinitrophenyl hydrazones.<sup>3</sup> Recently ion-exchange resins<sup>4</sup> have been found to be superior for the regeneration of carbonyl compounds from their nitrogenous derivatives. Although these methods are generally useful, most of the methods do not show selectivity

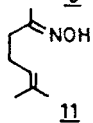
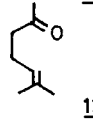
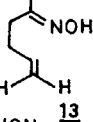
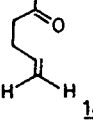


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\* To whom correspondence should be addressed.

towards any particular nitrogenous derivative and can not be applied with ease to molecules having multi-functional groups.

In connection with our studies on oxidative transformations we have recently developed a new reagent system, PDC/t-BuOOH, which has been found to be good for effecting allylic and benzylic oxidations.<sup>5</sup> In the course of further exploration on the usefulness of this reagent system, we find that a combination of PDC/t-BuOOH (1:1) is a convenient and highly selective reagent for the regeneration of ketones from ketoximes. Thus, treatment of a variety of ketoximes with four equivalents of PDC/t-BuOOH (1:1) at 0 °C for 2.5-4.5 h yielded the corresponding ketones in high yields. The results of such a methodology are summarised in the Table. There are a number of interesting features which are of particular interest. Although this reagent system has earlier been shown to be effective for allylic and benzylic oxidation,<sup>5</sup> ketoximes **7**, **9**, **11** and **13** underwent a facile deoximation without undergoing allylic or benzylic oxidation. The order of reactivity and hence the selectivity that can be achieved in the reaction of aldoximes is remarkable. For example, benzaldoxime **17** on treatment with PDC/t-BuOOH under the usual reaction conditions (3 h) underwent deoximation only to the extent of 5% and most

TABLE

Entry	Substrate	Time (h)	Product	Yield (%)
1	$\text{C}_6\text{H}_5-\overset{\text{NOH}}{\overset{\parallel}{\text{C}}}-\text{CH}_3$ <u>1</u>	3	$\text{C}_6\text{H}_5-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{CH}_3$ <u>2</u>	92
2	$p\text{-Br}-\text{C}_6\text{H}_4-\overset{\text{NOH}}{\overset{\parallel}{\text{C}}}-\text{CH}_3$ <u>3</u>	2.5	$p\text{-Br}-\text{C}_6\text{H}_4-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{CH}_3$ <u>4</u>	80
3	$\text{C}_6\text{H}_5-\overset{\text{NOH}}{\overset{\parallel}{\text{C}}}-\text{C}_6\text{H}_5$ <u>5</u>	4.5	$\text{C}_6\text{H}_5-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{C}_6\text{H}_5$ <u>6</u>	98
4	$\text{C}_6\text{H}_5-\overset{\text{NOH}}{\overset{\parallel}{\text{C}}}-\text{CH}_2\text{C}_6\text{H}_5$ <u>7</u>	4	$\text{C}_6\text{H}_5-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{CH}_2\text{C}_6\text{H}_5$ <u>8</u>	81
5	$\text{C}_6\text{H}_5(\text{CH}_2)_2-\overset{\text{NOH}}{\overset{\parallel}{\text{C}}}-\text{CH}_3$ <u>9</u>	3.5	$\text{C}_6\text{H}_5(\text{CH}_2)_2-\overset{\text{O}}{\overset{\parallel}{\text{C}}}-\text{CH}_3$ <u>10</u>	71
6	 <u>11</u>	4.5	 <u>12</u>	80
7	 <u>13</u>	4	 <u>14</u>	95
8	 <u>15</u>	2.5	 <u>16</u>	92
9	$\text{C}_6\text{H}_5\text{CH}=\text{NOH}$ <u>17</u>	3	$\text{C}_6\text{H}_5\text{CHO}$ <u>18</u>	5
		45	<u>18</u>	28
10	$m\text{-NO}_2-\text{C}_6\text{H}_4\text{CH}=\text{NOH}$ <u>19</u>	24	No reaction	-
11	$\text{CH}_3(\text{CH}_2)_6\text{CH}=\text{NOH}$ <u>20</u>	4.5	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$ <u>21</u>	9
12	$\text{C}_6\text{H}_5-\overset{\text{N}-\text{NHC}_6\text{H}_3(\text{NO}_2)_2}{\overset{\parallel}{\text{C}}}-\text{C}_6\text{H}_5$ <u>22</u>	36	No reaction	-

of **17** could be recovered unchanged. Even after treatment of **17** with excess reagent (6 eq.) and long reaction time (45 h) more than 70 % of the starting material remained unreacted. *m*-Nitro-benzaldoxime **19** did not show any appreciable reaction even after 24 h. Similar trend was observed in the reaction of aldoxime **20** derived from an aliphatic aldehyde. Most of the reagents available in the literature for effecting deoximation do not offer a selectivity of this type and hence the technique of selective deblocking of a ketone in the presence of an aldehyde can serve as an alternative to the Luche reaction.<sup>6</sup> It is also interesting to note that 2,4-DNP derivative **22** is inert to this reagent system. A number of methods of oxidative cleavage of C=N bond of oximes also affect C=N bond of 2,4-DNP derivatives. Here again the present methodology offers scope for further exploitation in organic synthesis.

### **Experimental**

The starting oximes and 2,4-dinitrophenyl hydrazones were prepared from the corresponding carbonyl compounds by known methods.<sup>7</sup> Octanaloxime was prepared following the reported procedure.<sup>8</sup> Pyridinium dichromate (PDC) was prepared by the reported procedure.<sup>9</sup> 70% *t*-butyl hydroperoxide (Koch Light Laboratories Ltd.) was used

as such. M.ps. were determined with a uni-melt capillary melting point apparatus and are uncorrected. B.ps. are uncorrected. Bulb to bulb distillation was carried out using Buchi GKR-50 distillation unit. Infrared (IR) spectra were recorded on Perkin-Elmer model 1320 and 580 spectrophotometers. Proton magnetic resonance (PMR) spectra were recorded at 90 MHz on a Varian EM-390 instrument and at 80 MHz on a Bruker WP-80 instrument.

**General procedure for the regeneration of carbonyl compounds from oximes:**

The oxidant was generated in solution by treating pyridinium dichromate (1.505 g, 4 mmol) and t-butyl hydroperoxide (0.36 g, 4 mmol, 0.38 mL) in dichloromethane (7.5 mL) for 15 min. at 0 °C. The dichloromethane layer was filtered over a cotton plug into another round bottomed flask kept at 0 °C. The reagent flask was rinsed with dichloromethane (2.5 mL) and filtered. To this, the carbonyl derivative (oxime, 1 mmol) in dichloromethane (2 mL) was added dropwise and the reaction mixture was stirred at 0 °C for 2h and then allowed to come to room temperature over a period of another 2 h. Dichloromethane was removed under vacuum and ether (15 mL) was added and filtered over a pad of Celite and the solvent was evaporated.

The crude product was purified by flash chromatography (ethyl acetate: petroleum ether, 1:9) to give the carbonyl compound which was compared with an authentic sample.

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