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# Selective Oxidation of Arylaldoximes by Cetyltrimethylammonium Dichromate to Arylaldehydes and Arylnitriles

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**Abstract:** Aldoxime is converted into corresponding nitrile derivative on treatment with cetyltrimethylammonium dichromate.

**Keywords:** Oxidation, arylaldoxime, cetyltrimethylammonium dichromate, arylnitrile

The conversion of oximes to nitriles have been carried out by using several dehydrating agents like trifluoroacetic anhydride, chlorosulphonyl isocyanate, diphosphorous tetraiodide, selenium dioxide, 4,6-diphenyl-2-methylthiopyrylium tetrafluoroborate, copper(II) acetate, and the triphenylphosphine/$CCl_4$.[1–4] Thionyl chloride has been used for conversion of oximes to nitriles in benzotriazole mixture[5] and on silica surface.[6] Appropriate non metal dehydrating agents have also been used for the conversion of nitriles from amides and oximes.[7] Ruthenium catalyst in benzene has also been used as a dehydrating agent during conversion of some sugar oximes and substituted arylaldoxime to corresponding nitriles.[8] In a photoregeneration reaction of carbonyl group from oxime, Lijser et al.[9] have obtained nitrile as a mixed product.

In continuation of our research in phase transferring oxidants[10,11] we wish to report the reaction of cetyltrimethylammonium dichromate (CTADC) with the oxime derivatives. For example, the oximes (**1**) on treatment with CTADC in presence of trace amount of acetic acid in dichloromethane gave

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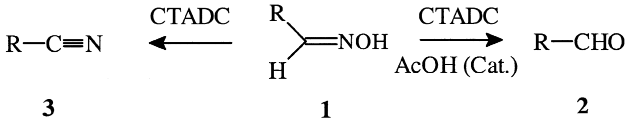
the corresponding aldehydes (**2**) (Table 2). The colour change from orange to green which suggested reduction of Cr(VI) to Cr(III). However, when the above reaction was performed in the absence of acetic acid, the corresponding nitrile derivatives (**3**) resulted (Table 1). The ketoximes remained unreacted under these reaction conditions. The nitriles and aldehydes were identified by comparison of melting/boiling points, IR and NMR spectral data with authentic samples. The carbonyl compounds were also characterized from the melting point of the 2,4-dinitrophenyl hydarazone derivatives and the IR spectral data.



**3** **1** **2**

## EXPERIMENTAL

The melting point and boiling point of the compounds were obtained by open capillary method. For the determination of boiling points of liquids Siwoloboff's method was used.[12] Oximes were prepared by standard method.[13] These are characterized from the melting point and IR spectral data. The IR spectra of the products were recorded on a Perkin Elmer RX-1 FTIR spectrometer in KBr disc for solids and in nujol for liquids. CTADC was synthesised by method reported earlier.[10,11]

### General Procedure for Oxidation of Oximes in Absence of Acetic Acid (Representative Procedure for Dehydration of *p*-Methoxybenzaldoxime)

A solution of CTADC (300 mg, 0.38 mmol) and *p*-methoxybenzaldoxime (200 mg, 1.3 mmol) in $CH_2Cl_2$ (25 mL) was refluxed for 4 h and concentrated.

***Table 1.*** Oxidation of oximes to corresponding nitriles by CTADC

| Sl. no. | Oxime | Product | Mp (s)/bp (l)[a] | Yield (%) |
|---|---|---|---|---|
| 1 | *o*-$OMeC_6H_4CH{=}NOH$ | *o*-$OMeC_6H_4CN$ | 137 (135) | 70 |
| 2 | *p*-$OMeC_6H_4CH{=}NOH$ | *p*-$OMeC_6H_4CN$ | 60 (57) | 85 |
| 3 | *o*-$NO_2C_6H_4CH{=}NOH$ | *o*-$NO_2C_6H_4CN$ | 106 (107) | 72 |
| 4 | *p*-$NO_2C_6H_4CH{=}NOH$ | *p*-$NO_2C_6H_4CN$ | 144 (146) | 86 |
| 5 | *m*-$NO_2C_6H_4CH{=}NOH$ | *m*-$NO_2C_6H_4CN$ | 117 (116) | 90 |
| 6 | *o*-$ClC_6H_4CH{=}NOH$ | *o*-$ClC_6H_4CN$ | 43 (46) | 80 |
| 7 | *p*-$ClC_6H_4CH{=}NOH$ | *p*-$ClC_6H_4CN$ | 89 (91) | 90 |
| 8 | *o*-$OHC_6H_4CH{=}NOH$ | *o*-$OHC_6H_4CN$ | 92 (95) | 78 |
| 9 | *p*-$OHC_6H_4CH{=}NOH$ | *p*-$OHC_6H_4CN$ | 110 (113) | 84 |

[a] The values given in the parentheses are the literature values.[14]

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***Table 2.*** Oxidation of oximes to the corresponding aldehydes and ketones by CTADC and acid

| Sl. no. | Oxime | Product | Reflux time (h) | Mp (s)/bp (1) | Yield (%) |
|---|---|---|---|---|---|
| 1 | *o*-$OMeC_6H_4CH{=}NOH$ | *o*-$OMeC_6H_4CHO$ | 6.0 | 238 (1) | 84 |
| 2 | *p*-$OMeC_6H_4CH{=}NOH$ | *p*-$OMeC_6H_4CHO$ | 5.0 | 249 (1) | 90 |
| 3 | *o*-$NO_2C_6H_4CH{=}NOH$ | *o*-$NO_2C_6H_4CHO$ | 3.0 | 45 (s) | 80 |
| 4 | *p*-$NO_2C_6H_4CH{=}NOH$ | *p*-$NO_2C_6H_4CHO$ | 2.5 | 105 (s) | 95 |
| 5 | *m*-$NO_2C_6H_4CH{=}NOH$ | *m*-$NO_2C_6H_4CHO$ | 4.5 | 57 (s) | 90 |
| 6 | *o*-$ClC_6H_4CH{=}NOH$ | *o*-$ClC_6H_4CHO$ | 2.5 | 215 (1) | 82 |
| 7 | *p*-$ClC_6H_4CH{=}NOH$ | *p*-$ClC_6H_4CHO$ | 1.5 | 46 (s) | 94 |
| 8 | *o*-$OHC_6H_4CH{=}NOH$ | *o*-$OHC_6H_4CHO$ | 1.0 | 198 (1) | 82 |
| 9 | *p*-$OHC_6H_4CH{=}NOH$ | *p*-$OHC_6H_4CHO$ | 1.5 | 114 (s) | 90 |
| 10 | $C_6H_{10}NOH$ | $C_6H_{10}O$ | 4.0 | 47 (s) | 88 |
| 11 | $C_6H_5C(CH_3){=}NOH$ | $C_6H_5C(CH_3){=}O$ | 2.0 | 203 (1) | 85 |
| 12 | $C_6H_5C({=}NOH)CH(OH)C_6H_5$ | $C_6H_5C({=}O)C({=}O)C_6H_5$ | 0.5 | 93 (s) | 91 |

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Ether was added to the residue, filtered and the filtrate evaporated to give *p*-methoxybenzonitrile (yield 85%), m.p. 60°C, lit.[14] m.p. 57°C, IR (KBr) $\nu$ cm$^{-1}$: 3392, 3102, 2223, 1605, 1509, 1257, 1175,1023, 829.

## General Procedure for Oxidation of Oximes in the Presence of Acetic Acid

A solution of CTADC (300 mg, 0.38 mmol), *p*-methoxybenzaldoxime (200 mg, 1.3 mmol) and acetic acid (0.5 mL) in $CH_2Cl_2$ (25 mL) was refluxed for 2 h and evaporated. The residue was then chromatographed on silica gel by using chloroform as an eluent to give *p*-methoxybenzaldehyde (yield, 90%) b.p. 249°C, m.p. of 2,4-dinitrophenylhydrazone, 251°C.[14]

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