Chromium Silicalite-2 (CrS-2): an Efficient Catalyst for the Direct Oxidation of Primary Amines to Nitro Compounds with TBHP†

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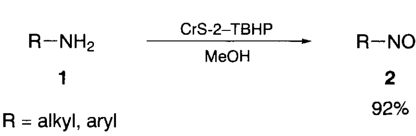
A chromium-containing medium-pore molecular sieve (Si:Cr > 140:1) having MEL (CrS-2) topology efficiently catalyses the direct oxidation of various primary amines to the corresponding nitro compounds using 70% *tert*-butyl hydroperoxide (TBHP) as the oxidant.

The direct oxidation of primary amines into the corresponding nitro derivatives is one of the most useful reactions for fundamental and industrial applications because it provides for the efficient preparation of many nitro compounds, which may otherwise be difficult to synthesize by direct nitration methods.[1] Previously, such oxidations under stoichiometric conditions have been performed mainly with peracetic acid, sodium perborate and dimethyl dioxirane[2] (for electron-donating substituents) or with peroxytrifluoroacetic acid and peroxydisulfuric acid[3] (for electron-deficient anilines). More recently, oxidants such as HOF–MeCN[4] and peroxotungstophosphate–H_2O_2[5] have been employed to effect the conversion of arylamines into nitroaromatics under homogeneous conditons. However, the difficulty in handling the hazardous nature of the anhydrous peracids and HOF coupled with the prototropic rearrangement of nitroalkanes into oximes make the existing methods[2–4] less than attractive.

The use of heterogenous catalysts in the liquid phase offers several advantages compared with their homogenous counterparts, *e.g.* ease of recovery and recycling, and enhanced stability.[6] Also, metal-catalysed oxidation of amines is of interest because of its relevance to the enzymatic degradation of nitrogen-containing compounds in biological systems. We report here that CrS-2 efficiently catalyses the oxidation of aliphatic and aromatic primary amines into the corresponding nitro derivatives with 70% TBHP as the oxidant (Scheme 1).

The zeolite CrS-2 was hydrothermally synthesized[7] using gels of the following compositions: $SiO_2 : xCr_2O_3$: 0.4TBAOH : 30 H_2O. Crystallization was performed at 443 K for 90 h. The crystalline material was subsequently calcined at 773 K for 5 h. The chemical analysis of the obtained CrS-2 sample gave an Si : Cr ratio of 140 : 1. This sample was further characterized[7] by XRD, IR, ESR and SEM techniques.

The results of CrS-2-catalysed oxidations of primary amines with 70% TBHP at 65 °C in MeOH as solvent are shown in Table 1. In a typical reaction procedure, a mixture of aniline (0.93 g, 10 mmol), CrS-2 (93 mg, 10% *m*/*m*) and 70% TBHP (4.5 ml, 33 mmol) in MeOH (25 ml) was heated under reflux for 4 h. After the reaction was complete (TLC), the catalyst was filtered off and the product purified by flash chromatography to afford nitrobenzene (1.13 g, 92%).



$$\underset{\substack{\mathbf{1}\\ R = \text{alkyl, aryl}}}{R{-}NH_2} \xrightarrow[\text{MeOH}]{\text{CrS-2–TBHP}} \underset{\substack{\mathbf{2}\\ 92\%}}{R{-}NO_2}$$

Scheme 1

Evidently, a variety of aromatic and aliphatic primary amines **1** are smoothly oxidized to the corresponding nitro compounds **2** in excellent yields on treatment with the CrS-2–TBHP system. It is also remarkable that arylamines with electron-withdrawing substituents such as COOH, NO_2, CN, *etc.* (Table 1, entries 2–5) are efficiently oxidized to the corresponding nitroarenes, which are otherwise difficult to obtain by the conventional nitration methods. The aliphatic primary amines possessing α-hydrogens underwent oxidation selectively to produce the corresponding nitro derivatives without undergoing any kind of prototropic rearrangement to oximes. However, it should be noted that benzylamine, under the reaction conditions given, gave only the benzaldoxime in 76% yield.

When the oxidation of aniline with TBHP was carried out with other metal-incorporated catalysts,[8] such as titanium silicate (TS-2) and vanadium silicate (VS-2), of similar topology, it was found that CrS-2 exhibits significantly better activity and selectivity (92%) than VS-2 (10%) while TS-2 totally failed to catalyse the reaction. Also when 30% H_2O_2 was used as the oxidant instead of 70% TBHP, the selectivity was considerably reduced and complex mixtures of products were obtained. In separate experiments, we have shown that both phenylhydroxylamine and nitrosobenzene are readily oxidized to nitrobenzene by CrS-2–TBHP, indicating that the reaction possibly proceeds through the intermediates hydroxylamine and nitrosoalkane. Mechanistically, the oxochromium(v) species present in the zeolite framework is believed to be responsible for amine-to-nitro oxidation. Work is in progress to gain further insight into the mechanistic aspect of this process.

In conclusion, we have shown that the oxidation of anilines with 70% TBHP catalysed by a stable, recyclable solid CrS-2 catalyst provides a simple, general procedure for the preparation of various substituted nitro compounds.

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Table 1 Direct conversion of primary amines into nitro compounds with TBHP catalysed by CrS-2[a]

Entry	Substrate **1**	*t*/h	Product[b] **2**	Yield[c] (%)
1	Aniline	4	Nitrobenzene	92
2	4-Aminobenzoic acid	5	4-Nitrobenzoic acid	60
3	4-Nitroaniline	6	1,4-Dinitrobenzene	65
4	2-Cyanoaniline	7	2-Cyanonitrobenzene	52
5	Methylanthranilate	5	Methyl 2-nitrobenzoate	91
6	4-Methoxyaniline	3	4-Methoxynitrobenzene	80
7	Cyclohexylamine	5	Nitrocyclohexane	85
8	1-Aminobutane	5	1-Nitrobutane	80
9	Benzylamine	4	Benzaldoxime	76

[a] No reaction in the absence of catalyst and the catalyst was recovered and reused 4 times without any loss of activity and selectivity. [b] Characterized by mp, IR, ^1H and ^{13}C NMR. [c] Isolated after chromatographic purification.

Footnote

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