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Efficient Oxidative Cleavage of Oximes to Their Corresponding Carbonyl Compounds with Chromic Acid Supported on Kieselguhr Under Heterogeneous Conditions

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Efficient Oxidative Cleavage of Oximes to Their Corresponding Carbonyl Compounds with Chromic Acid Supported on Kieselguhr Under Heterogeneous Conditions

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An efficient oxidative cleavage of oximes to their corresponding carbonyl compounds with chromic acid supported on kieselguhr reagent under heterogeneous conditions at reflux with a yield between 86 and 96% is described. In these reaction conditions, deoximation of aldoximes required a longer reaction time than that of ketoximes, and the conditions are not suitable for deoximation of aliphatic aldoximes.

Keywords carbonyl compounds, chromic acid, kieselguhr, oxidative cleavage, oximes

INTRODUCTION

Oxime compounds are useful protecting groups in organic syntheses[1] and have found extensive application in the isolation, purification, and characterization of carbonyl compounds.[2,3] Oximes have been used as intermediates for a number of synthetic products, and have proved to be important and useful reagents in organic syntheses as well.[4–6] The development of mild and efficient methods for the selective cleavage of derivatives containing a carbon–nitrogen double bond like oximes to afford carbonyl compounds continues to be a significant aspect of organic chemistry.

EXPERIMENTAL

Oxidative Cleavage of Benzophenone Oxime to Benzophenone: Typical Procedure

The chromium trioxide-kieselghur reagent[7] (450 mg) is placed in a flask together with dichloromethane (30 mL) and the mixture is magnetically stirred. A solution of benzophenone oxime (197 mg, 1 mmol) in dichloromethane (5 mL) is added, and after 2 h at reflux the solid is filtered and washed with dichloromethane (3 × 5 mL). The combined filtrates are evaporated to give crude product, which is purified by preparative thin-layer chromatography (TLC) with hexane:ethyl acetate (7:3) to afford 174 mg (96%) benzophenone.

RESULTS AND DISCUSSION

So far, many methods and reagents have been reported for regeneration of carbonyl compounds like aldehydes and ketones from oxime derivatives, for instance, mainly, hydrolytic, reductive, and oxidative reactions, and the deoximation process can be undertaken in both homogeneous and heterogeneous conditions.[8] It is well known that one of the most important procedures for this transformation is oxidation with hexavalent chromium derivatives, such as Jones reagent,[9], methylammonium chlorochromate–alumina,[10] chromium trioxide–silica gel,[11] pyridinium fluorochromate,[12] quinolinium dichromate,[13] potassium dichromate,[14] pyridinium fluorochromate–hydrogen peroxide,[15] 2,6-dicarboxypyridinium chlorochromate,[16] γ-picolinium chlorochromate,[16] benzyltriphenylphosphonium chlorochromate,[16] quinolinium fluorochromate,[19] tetramethylammonium fluorochromate(VI),[20] benzyltrimethylammonium fluorochromate(VI),[21] imidazolium dichromate,[22] dicarboxypyridinium fluorochromate,[23] tetrabutylammonium chromate,[24] chromic acid,[25] chromium trioxide–$NaHSO_4 \bullet H_2O$,[26] glycinium chlorochromate-silica gel,[27] ammonium chlorochromate–montmorillonite K10,[28] etc. Although some of the reported reactions with chromium(VI) or chromium(VI)-based reagents are carried out under mild conditions, most of these methods are often hazardous, expensive, or use reagents not readily available or reagents that need to be

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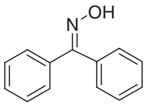
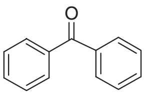
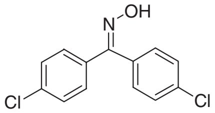
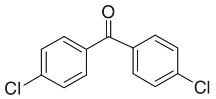
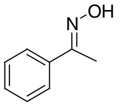
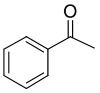
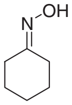
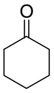
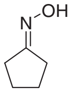
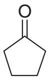
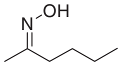
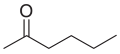
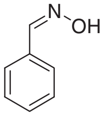
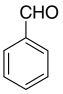
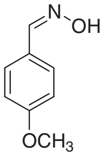
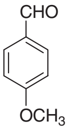
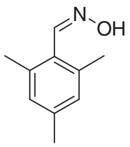
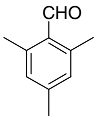
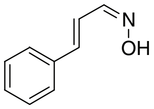
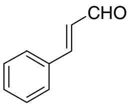
TABLE 1
Oxidative cleavage of oximes to their corresponding carbonyl compounds with chromic acid supported on kieselguhr reagent under heterogeneous conditions

Entry	Oxime	Time (h)	Product[a]	Yield[b] (%)
1		2		96
2		2		92
3		2.5		90
4		2.5		92
5		2.5		87
6		3		86
7		3		92
8		3		90
9		3		92
10		5		86

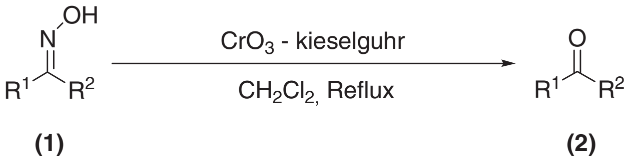
[a] All products were identified by comparison of their physical and spectral data with those of authentic samples.

[b] Isolated yields.

freshly prepared. Furthermore, some of these methods require long reaction times with poor yields of the products, or have tedious work-up procedures. Therefore, some existing procedures may be modified to more modern, elegant, and safe versions.

As a part of our ongoing program related to developing new oxidation methods and based on our previous investigations for oxidation of alcohols and α-hydroxy ketones with chromic acid supported on kieselguhr reagent,[7,29–31] we wish to report here a procedure for the oxidative cleavage of oximes (**1**) to their corresponding carbonyl compounds (**2**) with this reagent under heterogeneous conditions (Scheme 1). This procedure offers a simple and efficient deoximation method for the preparation of aldehydes and ketones, and is an extension of our previous work as well.

In this procedure, the mixture of oximes and chromic acid supported on kieselguhr reagent is heated under reflux in



SCH. 1.

dichloromethane, and a 1 to 1.5 molar ratio of the substrate to the oxidant is employed. The progress of the reaction is monitored with thin-layer chromatography (TLC), and the corresponding aldehydes and ketones are purified by preparative TLC in good yields. In the case of ketoxime, the starting materials are consumed in less than 3 h, and deoximation of aldoximes requires a slightly longer reaction time. However, these reaction conditions are not suitable for deoximation of aliphatic aldoximes.

Compared with some of the previous procedures for the oxidative cleavage of oximes to their corresponding carbonyl compounds with hexavalent chromium derivatives cited earlier, the main advantages of the present method are that the yield of most of the products is relatively higher and the reaction time of the oxidation is comparatively shorter. The oxidized products are all known compounds and identified by spectroscopic comparison with authentic samples. Our results are listed in the Table 1.

CONCLUSION

An efficient oxidative cleavage of oximes to their corresponding carbonyl compounds with chromic acid supported on kieselguhr under heterogeneous conditions at reflux with a yield between 86 and 96% is described. In case of ketoxime, the starting materials are consumed in less than 3 h, and deoximation of aldoximes requires a slightly longer reaction time. However, these reaction conditions are not suitable for deoximation of aliphatic aldoximes.

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