

An Improved Procedure for Oxidative Cleavage of Oximes to the Corresponding Carbonyl Compounds With Chromic Acid Supported on Kieselguhr Under Viscous Conditions

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An improved and efficient oxidative cleavage of oximes to the corresponding carbonyl compounds with chromic acid supported on kieselguhr reagent at room temperature under viscous conditions in the yield between 82% and 96% is described. The present procedure can overcome the problems that existed in the common solvent-free reactions as for the difficulty for the solid molecular collision to react.

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

INTRODUCTION

Oxime derivatives of carbonyl compounds are highly crystalline and are widely used for the characterization and purification of carbonyl compounds. The regeneration of carbonyl compounds from the corresponding oximes under mild conditions is important and of considerable interest. Therefore, the cleavage of these derivatives to the parent carbonyl compounds has been extensively investigated.^[1,2] So far, several procedures for the deoximation have been reported, for example, hydrolytic, oxidative, and reductive reactions^[3] and sometimes these transformations can be undertaken in both homogeneous and heterogeneous conditions. However, the development of milder and more 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.

One of the most important procedures for the deoximation process is oxidation with hexavalent chromium derivatives, such as Jones reagent,^[4] methylammonium chlorochromate-alumina,^[5] chromium trioxide-silica gel,^[6] pyridinium fluorochromate,^[7] quinolinium dichromate,^[8] potassium dichromate,^[9]

pyridinium fluorochromate-hydrogen peroxide,^[10] 2,6-dicarboxypyridinium chlorochromate,^[11] γ -picolinium chlorochromate,^[12] benzyltriphenylphosphonium chlorochromate,^[13] quinolinium fluorochromate,^[14] tetramethylammonium fluorochromate (VI),^[15] benzyltrimethylammonium fluorochromate (VI),^[16] imidazolium dichromate,^[17] dicarboxypyridinium fluorochromate,^[18] tetrabutylammonium chromate,^[19] chromic acid,^[20] chromium trioxide- $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$,^[21] glycinium chlorochromate-silica gel,^[22] and ammonium chlorochromate-montmorillonite K10.^[23] Although some of the reported chromium(VI) or chromium(VI)-based reagents are carried out under mild conditions, most of them are often hazardous, expensive, or use not readily available reagents or use reagents that are needed to be freshly prepared. Furthermore, some of these methods require long reaction times with the poor yields of the products, or have tedious workup procedures. Therefore, some existed procedures may be modified to more modern, elegant, and safe versions.

So far, a considerable attention has been paid to the solvent-free reactions in organic synthesis. Solvent-free reactions are not only of interest from ecological point of view, but in many cases also offer considerable synthetic advantages in terms of yield, selectivity, simplicity of the procedure, and operation at the room temperature. These factors are especially important in the industry. Unfortunately, under solvent-free conditions, in general, it is not satisfied for the reaction between solid substrates and solid reagents, such as oximes and chromium(VI) oxidants, performed at the room temperature because both of molecules are in crystal forms that are of difficulty for collision to reach the reaction, so that such reactions are normally carried out at the temperature near or over the substrate melting point by either heating or other technologies in advance in order to dissolve the solid substrates into the liquid forms to increase the reaction rate. Of those chromium(VI) or chromium(VI)-based reagents for the oxidation of oximes described above only a few experiments were carried out under solvent-free conditions,^[9,18] and basically the reaction procedure is that the solid mixture of substrate and oxidants in a mortar was ground with a pestle and

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then the products were produced, which can be performed in the laboratory but might be not satisfied to carry out in a large scale.

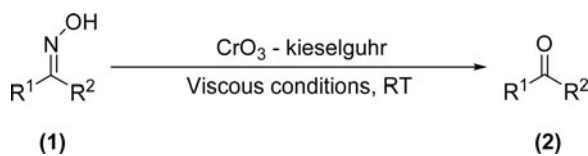
EXPERIMENTAL

Oxidative Cleavage of Benzophenone Oxime to Benzophenone: Typical Procedure

Benzophenone oxime (197 mg, 1 mmol) was dissolved in dichloromethane (0.2 mL) to form a viscous liquid, and then chromium trioxide-kieselguhr^[26] (450 mg, kieselguhr purchased from Tianjin Fu Chen Chemical Reagent Factory) was added. The mixture was shaken mechanically at room temperature. The progress of the reaction was monitored by TLC (silica gel GF₂₅₄) using hexane:ethyl acetate (7:3) as eluent. After 4 h the reaction mixture was washed with dichloromethane (3 × 10 mL). The combined filtrates were evaporated to give crude product, which was purified by preparative TLC (silica gel GF₂₅₄) with hexane:ethyl acetate (7:3) to afford benzophenone (172 mg; 95%).

RESULTS AND DISCUSSION

We have described oxidative cleavage of oximes to the carbonyl compounds with chromic acid supported on kieselguhr reagent at reflux under heterogeneous conditions,^[24] and oxidation of benzoin to the benzil with manganese dioxide at room temperature under viscous conditions.^[25] In continuation of previous work,^[24,25] we now report here an improved and more efficient procedure for the oxidation of oximes (**1**) to the corresponding aldehydes and ketones (**2**) using chromic acid supported on kieselguhr at room temperature under viscous conditions (Scheme 1), which can overcome the problems existed in the common solvent-free reactions of the difficulty for the solid molecular collision to react. The present procedure offers a simple and efficient oxidation method for the regeneration of carbonyl compounds from the corresponding oximes.



SCH. 1.

Under our experiments, some typical oximes were oxidized and 1 to 1.5 molar ratio of the substrate to the oxidant (50% w/w; chromium trioxide to kieselguhr^[26]) was employed. The oxidation was very simple: first the solid substrate was dissolved with a very minimum amount of dichloromethane to form a viscous liquid, and then the oxidant was added in one portion. The mixture was shaken magnetically at room temperature until thin-layer chromatography (TLC) analysis indicated a completed reaction, and the product was then purified by preparative TLC. All the reactions were completed within 4.5 h. The results,

which are described in Table 1, show that it is an efficient oxidation route for oximes, and gives the corresponding carbonyl compounds in high yields. The oxidized products are all known compounds and identified by spectroscopic comparison with authentic samples.

The main advantages of the present procedure are that under viscous conditions the oxidation of the solid substrates can be carried out very efficient with mild process. As an example, the results for oxidation of benzaldehyde oxime to benzaldehyde

TABLE 1
Oxidative cleavage of oximes to the corresponding carbonyl compounds with chromic acid supported on kieselguhr under viscous conditions

Entry	Oxime	Time (h)	Product ^a	Yield ^b (%)
1		4		95
2		4		86
3		4.5		90
4		4.5		86
5		4		82
6		3.5		95
7		4		92
8		4		96
9		3.5		86

^aAll products were identified by comparison of their physical and spectral data with those of authentic samples.

^bYield of isolated pure product.

TABLE 2
Comparison of oxidation of benzaldehyde oxime to benzaldehyde with chromium trioxide-kieselguhr reagent under different reaction conditions

Entry	Reaction conditions	Molar ratio substrate to chromium trioxide	Reaction time (h)	Yield (%)	References
1	Viscous conditions/RT	1:1.5	3.5	95	This work
2	CH ₂ Cl ₂ /reflux	1:1.5	3	92	24

using chromic acid supported on kieselguhr under different reaction conditions are compared (Table 2). From this table it is shown that even for the similar yields obtained of the product and the similar reaction time used, the reaction under heterogeneous conditions was performed at reflux (entry 2), while it under viscous conditions was at room temperature (entry 1). In addition to milder reaction conditions, because the present oxidation was carried out under a very minimum amount of solvents, the contamination, toxicity, and environmental pollution of the solvents were largely decreased. Overall, the benefits of the current procedure are over those of some reported methods using chromium(VI)-based reagents as oxidants.

CONCLUSION

An improved and efficient procedure for oxidative cleavage of oximes to the corresponding aldehydes and ketones using chromic acid supported on kieselguhr reagent under viscous conditions at room temperature is described, which can overcome the problems existed in the common solvent-free reactions of the difficulty for the solid molecular collision to react.

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