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A Facile Procedure for the Conversion of Oximes to Ketones and Aldehydes by the Use of Jones Reagent Adsorbed on Kieselguhr Reagent

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An efficient oxidation of oximes to their corresponding ketones and aldehydes with Jones reagent supported on kieselguhr under heterogeneous conditions at room temperature in the yield between 84 and 93% is described. The present procedure is an extension of application of Jones reagent supported on kieselguhr.

Keywords carbonyl compounds, Jones reagent, kieselguhr, oxidation, oximes

INTRODUCTION

Oxime derivatives of carbonyl compounds are highly crystalline and are widely used for the characterization and purification of carbonyl compounds. Therefore, the regeneration of carbonyl compounds under mild conditions is important and of considerable interest, and extensive investigations on the cleavage of these derivatives to the parent carbonyl compounds have been investigated.[1,2] So far, several such procedures for this transformation have been reported, for example, hydrolytic, oxidative, and reductive reactions,[3–11] and sometimes the deoximation process can be undertaken in both homogeneous and heterogeneous conditions. Even though some of the known methods or reagents are carried out under mild reaction conditions, most of them require drastic conditions, high temperature, long reaction times, or unreadily available reagents, and have tedious work-up procedures. Therefore, the development of mild and efficient methods for the selective cleavage of derivatives containing a carbon-nitrogen double bond such as oximes to afford carbonyl compounds continues to be a significant aspect of organic chemistry.

Until now, hexavalent chromium derivatives have been used for the selective oxidative cleavage of regeneration of carbonyl compounds from oximes. The utility of chromium (VI) reagents in the deoximation transformation has some limitations especially owing to their selectivity and inherent toxicity. Jones reagent is one of the best known chromium (VI) reagents for the oxidations of secondary alcohols to ketones, but it fails to produce satisfactory results for oxidation of primary alcohols, including benzyl alcohols to the corresponding aldehydes. This problem in the oxidation reaction arises due to the fact that aldehydes react with water and alcohols under acidic aqueous media employed in the Jones oxidation procedure, producing hydrates and hemiacetals, which are then oxidized to carboxylic acids and esters, respectively.[12] In addition, Jones reagent has not been widely used in organic synthesis because they have the potential health hazards from handling this reagent, the problems in disposal of the toxic chromium compounds, the by-product produced in the oxidation, and the difficulty in product isolation. However, it seems that these disadvantages might be overcome by the way of using supported reagent technique.[13,14]

It is well known that many organic reactions have been devised in which the reagents are deposited on various inorganic solid supports. These novel reagents have advantages over the conventional homogeneous solution techniques, for instance, ease of setup and of work-up, mild experimental conditions, and gain in yield and/or selectivity.

EXPERIMENTAL

Oxidative Cleavage of Benzophenone Oxime to Benzophenone, Typical Procedure

To a vigorously stirred kieselguhr (1 g) Jones reagent[12] (0.24 mL, 2 mmol) is added slowly. CH_2Cl_2 (26 mL) is added to the obtained mixture. A solution of benzophenone oxime (197 mg, 1 mmol) in CH_2Cl_2 (2 mL) is then added slowly to the previous stirred heterogeneous mixture at room temperature for 1.5 h. The progress of the reaction is monitored by TLC using hexane-ethyl acetate (8:2) as eluent. The solid is filtered and washed with CH_2Cl_2 (3 × 5 mL). The combined filtrates are evaporated to give crude product, which is then purified by preparative TLC with hexane:ethyl acetate (7:3) to afford 163 mg (90%) benzophenone.

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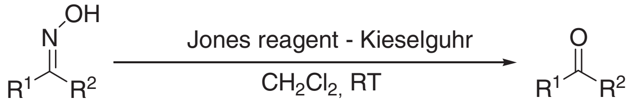
RESULTS AND DISCUSSION

Previously, we have reported an efficient method for the selective oxidation of alcohols to their corresponding carbonyl compounds by using Jones reagent supported on kieselguhr.[14] In continuation of this study, we are interested in extending the applicability of this reagent system to the oxidation of other functional groups. Therefore, we now report here in using Jones reagent supported on kieselguhr for the oxidative cleavage of oxime derivatives (**1**) to the corresponding aldehydes and ketones (**2**) under heterogeneous conditions at room temperature (Scheme 1).

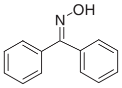
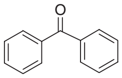
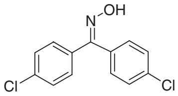
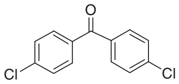
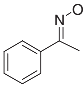
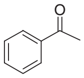
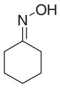
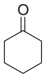
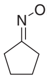
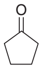
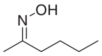
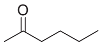
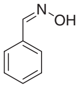
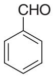
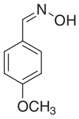
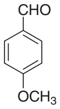
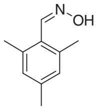
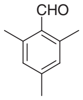
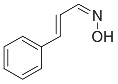
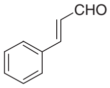


(1) **(2)**

SCH. 1.

Under our experiments, a 1 to 2 molar ratio of the substrate to Jones reagent supported on kieselguhr is employed. The mixture of oximes and oxidant is stirred in dichloromethane at room tem-

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

Entry	Oxime	Time (h)	Product*	Yield** (%)
1		1.5		90
2	 	1.5	 	93
3		1.5		92
4		1.5		92
5		1.5		85
6		2		86
7		2	 	90
8	 	2	 	90
9		2	 	86
10		2	 	84

*All products were identified by comparison of their physical and spectral data with those of authentic samples. **Yield of isolated pure product.

perature and all oxidation are completed within 2 h. The progress of the reaction is monitored with TLC, and the corresponding aldehydes and ketones are obtained in good yields by purification with preparative TLC. The main advantages of the present oxidation are that the insoluble solid support, kieselguhr, provides a particular reaction environment capable of enhancing the reaction selectivity and reactivity, and the present procedure is an extension of application of this reagent as well. The oxidized products are all known compounds and identified by spectroscopic comparison with authentic samples. Our results are listed in Table 1.

CONCLUSION

Efficient oxidative cleavage of oximes to their corresponding carbonyl compounds with Jones reagent supported on kieselguhr under heterogeneous conditions at room temperature in the yield between 84 and 93% is described. The present procedure is an extension of application of Jones reagent supported on kieselguhr.

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