Regeneration of Carbonyl Compounds from Oximes Using BTBAD under Microwave Irradiation

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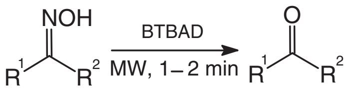
Bis-tetrabutylammonium dichromate (BTBAD) has been found to be an efficient and new reagent for the conversion of oximes to the corresponding carbonyl compounds. The reaction was performed under microwave irradiation and gave excellent yields. It also facilitates the de-protection of acetals and ketals.

There is a growing interest for generating carbonyl compounds from oximes since these can be prepared from non-carbonyl precursors as well as used for the protection and purification of carbonyl compounds.[1] Conversion of oximes back to their corresponding carbonyl compounds is a very important process in synthetic organic chemistry. Several oxidative de-oximation methods have been developed and have found some definite advantages over the conventional methods.[2,3]



Here, we report the conversion of oximes to the corresponding carbonyl compounds using BTBAD as a reagent in dichloromethane. BTBAD has been already reported to be an oxidizing agent in the conversion of alkyl halides to carbonyl compounds. This reagent is readily prepared by stirring a heterogeneous mixture of tetrabutylammonium hydrogen sulphate in dichloromethane and potassium chromate in water at room temperature for 2 h.[4] BTBAD was obtained from the organic layer as orange crystals (97% yield).

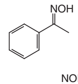
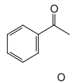
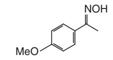
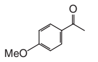
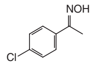
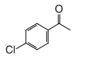
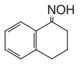
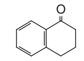
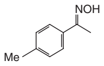
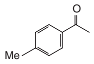
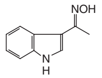
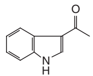
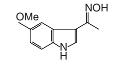
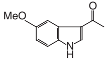
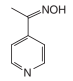
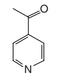
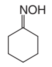
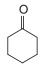
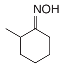
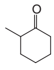
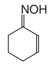
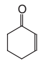
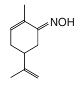
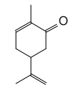
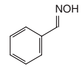
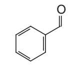
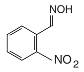
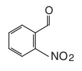
Microwave irradiation techniques are being extensively used by the organic chemists to augment reaction rates. Microwave assisted reactions are essentially easy to handle and demand less tedious work-up procedures.[6] Solvents with higher dielectric constants are favoured in a microwave procedure as they are proved to increase yields.[6] Therefore, we have chosen dichloromethane which has a higher dielectric constant over many other solvents.

The de-oximation was performed by mixing one equivalent of the reagent with one equivalent of the oximes in a mortar and ground with pestle until the formation of a homogeneous mixture. The reaction mixture was dissolved in dichloromethane and then transferred to an Erlenmeyer flask and irradiated in a microwave oven, until complete disappearance of the starting material.

We also rationalized that since it could cleave the oximes, it could have a similar effect in deprotecting the acetals and ketals for generation of carbonyl compounds. Deprotection of acetals and ketals have been studied extensively by various methods.[7] This reaction is of considerable importance in many transformations.

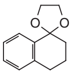
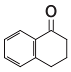
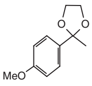
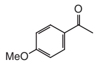
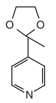
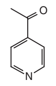
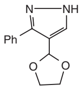
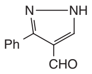
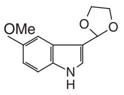
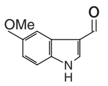
BTBAD is an efficient and novel reagent for the oxidative cleavage of C=N bond of oximes under microwave irradiation. Using this reagent under microwave irradiation, various oximes have been successfully converted to their corresponding aldehydes and ketones in excellent yields of 85–95% within time periods of 1–2 min. The corresponding carbonyl compound appeared as the sole product and no by-products were observed. The same procedure was adopted for the acetals and ketals,

Table 1. Oxidative cleavage of oximes with BTBAD under microwave irradiation[a]

Entry	Oxime	Product	Time /s	Yield[b] /%
1			60	94
2			75	93
3			75	90
4			120	89
5			60	92
6			120	87
7			120	89
8			60	92
9			120	87
10			120	89
11			120	85
12			120	87
13			60	93
14			60	92

[a] Products were confirmed by comparison with authentic sample (TLC, IR, NMR, and (solid) m.p).
[b] Yield of isolated pure carbonyl compound.

Table 2. Oxidative cleavage of ketals and acetals with BTBAD under microwave irradiation[a]

Entry	Acetal/ketal	Product	Time /s	Yield[b] /%
1			120	85
2			120	89
3			120	92
4			120	90
5			120	87

[a] Products were confirmed by comparision with authentic sample (TLC, IR, NMR, and (solid) m.p).

[b] Yield of isolated pure carbonyl compound.

and the reaction was found to complete in 2 min. The pure carbonyl compound was characterized by IR, ^{1}H NMR, and melting point analysis.

In conclusion, we report a new and efficient methodology for the regeneration of aldehydes and ketones from oximes under microwave irradiation. It is also found to facilitate deprotection of acetals and ketals. The main advantage of this new method includes the availability of inexpensive BTBAD as a catalyst, mild reaction conditions and reduced reaction times with excellent yields.

The reaction was carried out in the domestic microwave oven, BPL microwave model BMO-700T, manufactured by BPL-SANYO, India. Acetophenone oxime (1.48 mmol) and BTBAD (1.48 mmol) was ground with pestle in a mortar to form a homogeneous mixture, then transfered to an Erlenmeyer flask in a microwave oven, until TLC showed complete disappearance of starting materials. CH_2Cl_2 was added to the reaction mixture, concentrated, charged on small silica gel column and eluted with a mixture of EtOAc-petroleum ether (2:8) to afford the pure product in 94% yield (Table 1). The same procedure was adopted for the ketals and the yields are given in Table 2.

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