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Regeneration of Carbonyl Compounds from Oximes under Microwave Irradiations

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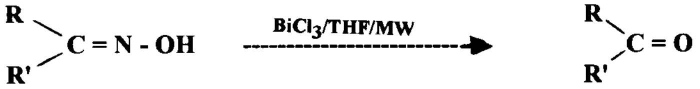
Abstract: A new and efficient method for the cleavage of oximes **1** has been achieved by a simple reaction of a ketoxime or an aldoxime with bismuth trichloride in tetrahydrofuran under microwave irradiations.

Regeneration of carbonyl compounds from their oximes is an important reaction, and assumed added importance after the discovery of the Barton reaction[1] in which oximes are produced at non-activated hydrocarbon sites. An efficient catalytic cleavage of oximes would therefore be of considerable benefit. Although literature enumerates quite a number of methods for the conversion of oximes into carbonyl groups, careful scrutiny of the reaction procedures reveals some shortcomings or other in most of the procedures. Benzaldoxime, for example, was deoximated in poor yield by pyridinium chlorochromate[2], in 35% yield by pyridinium chlorochromate-hydrogen peroxide[3], in 56% yield by triethylammonium chlorochromate[4] and in 72% yield by chromic anhydride-chlorotrimethyl silane[5]. Methods so far developed to regenerate carbonyl compounds from oximes consist of hydrolytic (acid-catalysed[6]), or oxidative[7], or reductive[8] reactions and most of them are noncatalytic. In view of the current thrust on catalytic processes[9], there is merit in developing a truly catalytic cleavage of oximes using inexpensive and non-polluting reagents. Herein we wish to report the use of bismuth trichloride as a new catalyst for the cleavage of oximes under microwave irradiation[10]. The reaction proceeds efficiently in high yields at ambient pressure within a few minutes[11].



1 2

In a typical procedure, benzophenone oxime **1** (10 mmol) and bismuth trichloride[12] (0.32g, 1 mmol) were mixed together in tetrahydrofuran (10ml) in an Erlenmeyer flask and placed in a commercial microwave oven (operating at 2450 MHz frequency) and irradiated for 2 mins. The reaction mixture was allowed to reach room temperature, treated with water and extracted with dichloromethane. Removal of solvent and the residue on purification by column chromatography on silica gel gave the corresponding benzophenone **2** in 96% yield and there was no evidence for the formation of any side products. Similar treatment of other oximes gave the corresponding carbonyl compounds **2** in 70-96% yields as summerised in the table. The reaction was not equally effective when acetophenone oxime was reacted thermally in tetrahydrofuran without microwave energy. The clevage of oxime was only 40% after 10 hours of refluxing. All the compounds obtained were characterised by infrared and ^{1}H NMR spectroscopy and finally by comparison with authentic samples.

The table shows some of the aldehydes and ketones regenerated from the corresponding oximes under microwave irradiations. The rate of catalytic cleavage of benzophenone oxime was fast, requiring 0.1 equivalent of the catalyst and needing only 2 mins. to complete the reaction. Even the sterically hindered camphor oxime was converted to camphor in high yields. Interestingly, oximes of α,β-unsaturated carbonyl compounds were not successfully deoximated. Cinnamaldehyde oxime for example, produced a mixture of products in moderate yields. Presumably, the yields from the aldoximes were comparatively low due to the over oxidation of the regenerated aldehydes. It should be also noted that this reagent gave a much better results in the conversion of cholestan-3-one oxime to the parent ketone in comparison with periodic acid[13].

In conclusion, the present procedure for the regeneration of carbonyl compounds has some advantages over the existing methods and will make a useful and important addition to the present methodologies. The main advantages of this new method are mild reaction conditions, reduced reaction times, minimisation of side products and excellent yields.

Table: Bismuth trichloride catalysed cleavage of oximes **1** under microwave irradiations

Entry	Substrate **1**	Time/mins.	Product **2**	Yield[a](%)
1	Acetophenone oxime	5	Acetophenone	80
2	Cyclohexanone oxime	4	Cyclohexanone	82
3	Camphor oxime	6	Camphor	83
4	Benzophenone oxime	2	Benzophenone	96
5	1-Tetralone oxime	5	1-Tetralone	86
6	4-Methylacetophenone oxime	3	4-Methylacetophenone	80
7	4-Chlorobenzaldoxime	3	4-Chlorobenzaldehyde	70
8	4-Methoxybenzaldoxime	4	4-Methoxybenzaldehyde	72
9	4-Methoxybenzophenone oxime	3	4-Methoxybenzophenone	85
10	Cholestan-3-one oxime	5	Cholestan-3-one	80
11	Cinnamaldehyde oxime	5	Cinnamaldehyde	45[b]

[a]Yields refer to pure isolated products, characterised by IR, ^{1}H NMR and MS. [b]Further increasing the reaction time gave no significant improvement in yields but rather decomposition occurred.

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