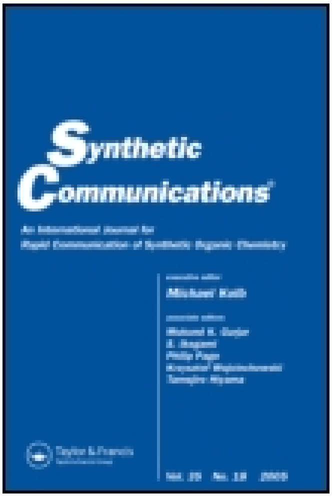

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A Novel Transformation of Oximes into Hydrazones by Hydrazine Hydrate

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A Novel Transformation of Oximes into Hydrazones by Hydrazine Hydrate

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ABSTRACT

We report a novel transformation of different substituted aryl, diaryl, and aralkyloximes into the respective hydrazones using hydrazine hydrate in ethanol at reflux in excellent yields.

Key Words: Oximes; Hydrazine hydrate; Hydrazones.

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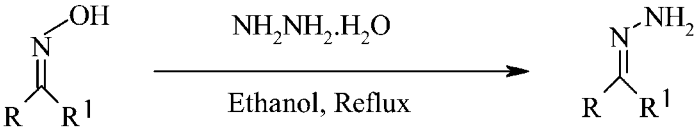
Oximes, being highly stable and readily prepared compounds, are very useful not only for isolation, purification, and characterization of carbonyl compounds, but also for protection of a carbonyl group.[1] Numerous methods have been developed for their oxidative,[2] reductive,[3] and hydrolytic[4] conversion to carbonyl compounds. Dehydration to nitriles,[5] reduction to amines,[6] and acylation of oximes[7] are also documented in the literature.

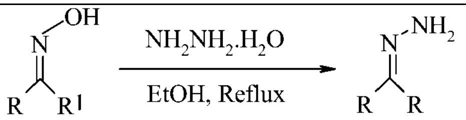
On the other hand, hydrazones are versatile intermediates and important building blocks. They have been prepared by treating aryl hydrazines with carbonyl compounds using a variety of solvents in presence or absence of an acidic catalyst.[8] Since oximes can be prepared from noncarbonyl starting materials,[9–11] it would be very interesting to develop a method to convert oximes into hydrazones, which would constitute the first procedure for obtaining hydrazones from noncarbonyl compounds. This communication reports the conversion of aryloximes into the corresponding hydrazones (Sch. 1).

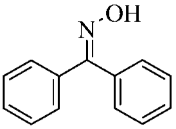
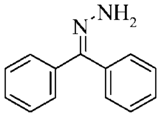
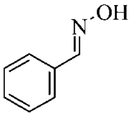
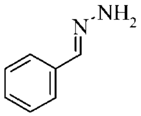
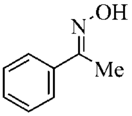
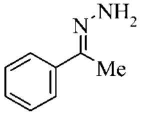
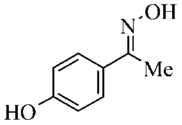
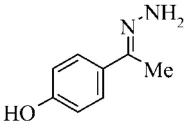
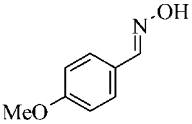
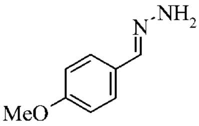
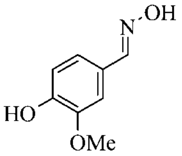
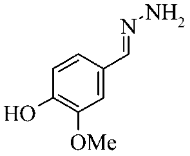
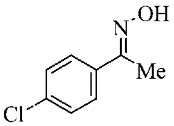
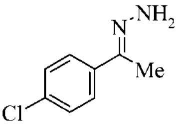
In a typical experiment, benzophenone oxime (1.97 g, 10 mmol), 99–100% hydrazine hydrate (2 mL), and ethyl alcohol (15 mL) were heated under reflux for 1 h (disappearance of the starting material on TLC), and the reaction mixture was diluted with water and extracted with ether. Removal of ether provided benzophenone hydrazone purified by silica gel column chromatography using 10% ethyl acetate in light petroleum to get benzophenone hydrazone (1.82 g, 95%). The product was identified by its mp, IR, and NMR spectra. Encouraged by this result, we extended this reaction to substituted oximes, in order to verify the suitability of the method for the conversion of oximes into the respective hydrazones. The results are summarized in Table 1. While diaryl and arylalkyl oximes furnish the expected hydrazones, dialkyl oximes such as camphor oxime, carvone oxime, and cyclohexyl oxime give a complex mixture of products under the above reaction conditions. A plausible mechanism for the formation of hydrazones as shown in Sch. 2 has been proposed for the reaction.



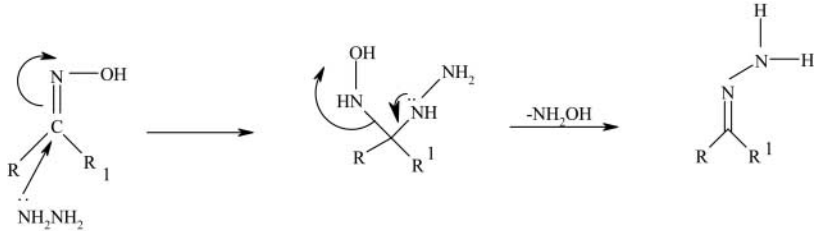
Scheme 1.

Table 1. Conversion of oximes into the corresponding hydrazones by hydrazine hydrate/EtOH at reflux.



Entry	Oxime	Hydrazone	Time (h)	Yield (%)
1			1.00	95
2			1.20	92
3			1.20	94
4			1.25	95
5			1.20	93
6			1.50	86
7			1.25	88

Products were characterized by GC, IR, and ^1H NMR; yields are based on TLC and GC analysis.



Scheme 2.

CONCLUSION

In conclusion, we have developed the first method to convert oximes into corresponding hydrazones.

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