Asian Journal of Chemistry; *Vol. 24, No. 3 (2012), 1354-1356*

ASIAN JOURNAL OF CHEMISTRY

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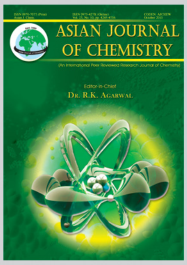

Oximation of Carbonyl Compounds by Basic Alumina Supported Amberlite IRA 400 Under Microwave Energy and Pestle/mortar

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(*Received*: 2 May 2011; *Accepted*: 12 November 2011) AJC-10659

An efficient and novel method for the preparation of oximes from carbonyl compounds under solventless conditions.

Key Words: Carbonyl compounds, Resin, Microwave radiation, Pestle/mortar.

INTRODUCTION

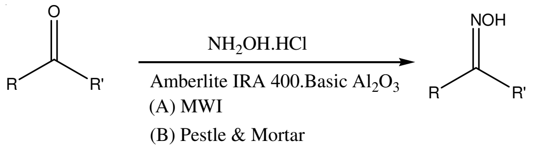
Conversion of carbonyl functionality into oximes is an important reaction in synthetic organic chemistry, not only for protection[1], purification and characterization of carbonyl groups, but also for various functional group transformations such as nitriles[2], nitro compounds[3], nitrones[4], amines[5], isoxazolines[6], lactams, carboxylic acids and amides. Since ketones are poor radical acceptors that readily undergo reductive cyclization to afford compounds containing C-N single bonds[7], thus, different and better methods for the preparation of oximes are constantly being developed. Conventionally, oximes are prepared[8] by refluxing an alcoholic solution of carbonyl compound with hydroxylamine hydrochloride and pyridine. More recently oximes have been synthesized using cerium sulphate[9], calcium oxide[10], amberlyst A-21[11] *etc.*

EXPERIMENTAL

All the chemicals have been purchased from Sigma Aldrich. IR spectra were determined on a Perkin-Elmer Model 1430 spectrometer. ^{1}H NMR spectra were recorded using 300 MHz spectrometer. Chemical shift (δ) are reported in ppm with tetramethylsilane as internal standard.

Method A: A mixture of 4-nitrobenzaldehyde (1, 0.1 g, 0.66 mmol), hydroxylamine hydrochloride (0.1 g, 1.44 mmol) and alumina supported amberlite IRA-400 resin (0.12 g) were exposed to microwave radiations at 75 % power level and temperature 45 °C in a multimode plasamatronic microwave for 5 min. On cooling, the reaction mixture was extracted with diethyl ether (2 × 10 mL) and the combined organic phase was washed with water (2 × 10 mL), brine and dried. Evaporation of the solvent *in vacuo* afforded the pure oxime (2, 0.10 g, 96 %), m.p. 123-127 °C.

Method B: A mixture of 4-nitrobenzaldehyde (1, 0.1 g, 0.66 mmol), hydroxylamine hydrochloride (0.1 g, 1.44 mmol) and alumina supported amberlite IRA-400 resin (0.12 g) was ground in a pestle and mortar for 8 min. The progress of the reaction was monitered by TLC. The reaction mixture was then taken in diethyl ether (2 × 15 mL) and filtered and the filtrate was washed with water (2 × 10 mL), brine and dried followed by evaporation of the solvent *in vacuo* to furnish the pure aldoxime (2, 0.076 g, 70 %) (**Scheme-I**).



Scheme-I R = Ar, aliphatic; R' = H, aliphatic

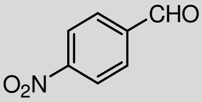
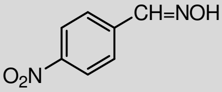
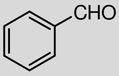
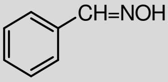
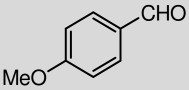
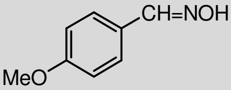
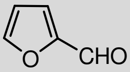
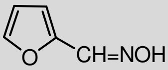
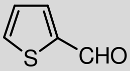
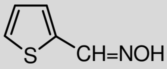
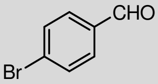
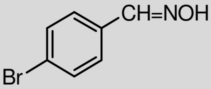
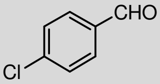
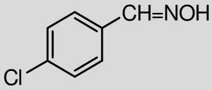
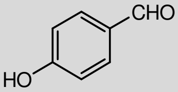
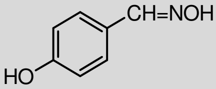
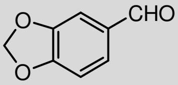
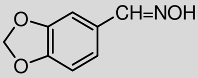
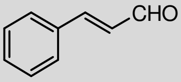
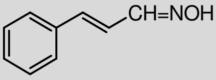
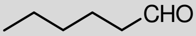
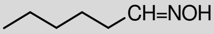
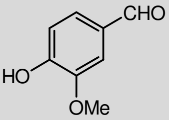
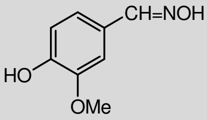
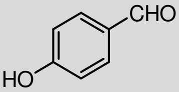
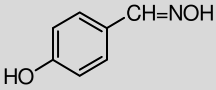
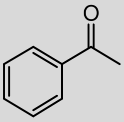
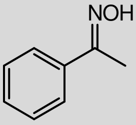
4-Nitrobenzaldehyde oxime (2): m.p. 123-127 °C. IR (CCl_4)/ν_{max} cm^{-1} : 3200, 3100, 1630, 1600, 1500, 1330, 860, 840. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.5-7.8 (m, 4H, ArH), 8.6 (s, 1H, -CH=NOH), 8.3 (bs, 1H, -CH=NOH, D_2O exchangeable).

RESULTS AND DISCUSSION

In adherence to the new concept of green chemistry solid supports are replacing more and more organic solvents for conducting chemical reactions talking into account the environmental concerns and the aspect of cost, safety and simple operation.

Our endeavoring efforts for providing ecofriendly and non-toxic methods for carrying chemical reactions have led us to develop novel, environmentally safe and clean synthesis of aldoximes and ketoximes using microwave as well as by

TABLE-1
OXIMATION OF ALDEHYDES AND KETONES USING BASIC ALUMINA SUPPORTED AMBERLITE IRA 400

Entry	Reactant	Product	Time[a] (min)	Yield[a] (%)	Time[b] (min)	Yield[b] (%)
1.	 **1**	 **2**	5	96	8	70
2.	 **3**	 **4**	5	88	8	81
3.	 **5**	 **6**	3	86	7	78
4.	 **7**	 **8**	4	83	8	77
5.	 **9**	 **10**	5	75	8	74
6.	 **11**	 **12**	4	78	8	83
7.	 **13**	 **14**	5	74	8	70
8.	 **15**	 **16**	4	85	7	74
9.	 **17**	 **18**	5	90	7	85
10.	 **19**	 **20**	6	94	8	79
11.	 **21**	 **22**	4	88	8	84
12.	 **23**	 **24**	5	87	7	79
13.	 **25**	 **26**	4	92	8	83
14.	 **27**	 **28**	6	70	9	55

[a]Method-A, [b]Method-B

grinding in a mortar. In one set of experiments, the reagents and basic alumina supported amberlite-400 were subjected to microwave radiation at 70-80 % power level and 45-70 ºC temperature for 3-6 min to provide corresponding oximes in good yields (70-96 %) (Table-1). The second set of experiments makes use of local heat produced by grinding of the reactants along with basic alumina supported amberlite-400 in a mortar for driving the chemical reaction to afford the product in moderate to good yields (55-85 %).

The oximes were characterized by IR and ^{1}H NMR spectral analysis. ^{1}H NMR spectra of the oximes showed the presence of a singlet between δ 7.8-8.7 (R-CH=NOH, exchangeable with D_2O). IR spectra recorded prominent absorption bands between 1680-1630 cm^{-1} ν(C=N). Further confirmation about the formation of oximes was arrived at by the absence of singlet between δ 9.8-10.4 (-CHO) in the ^{1}H NMR spectra and also by the absence of IR absorption bands in the region 1715-1695 cm^{-1} ν(C=O).

Conclusion

It is a effective methodologies for the preparation of oximes from aldehyde and ketone and noticeable features are eco-friendly, easy to handle, employ shorter reaction times and solventless conditions.

ACKNOWLEDGEMENTS

The authors thank D.S. College, Aligarh for laboratory facilitites.

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