Catalytic effect of wet molecular sieve 3Å in dry media on syntheses of oximes and 1,3-dioximes

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A simple, efficient and eco-friendly method has been developed for the condensation of hydroxylamine hydrochloride with aldehydes, ketones and 1,3-diketones in the presence of powdered molecular sieves (3Å) as catalyst. Aldoximes, ketoximes and 1,3-dioximes were obtained in excellent yields.

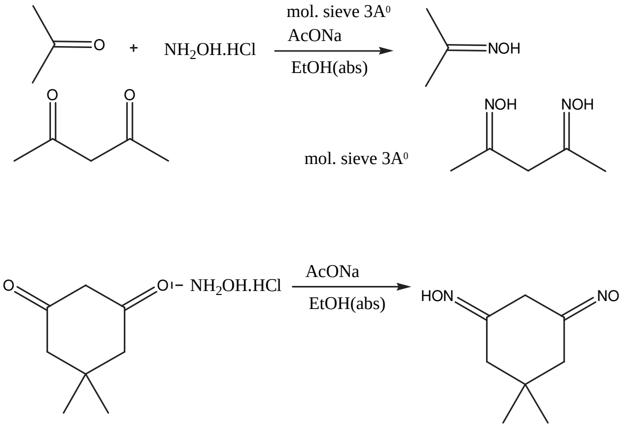
Keywords: oximes, 1,3-dioximes, 1,3-diketones, molecular sieve (3Å), dry media

Oximes are one of the most important families of organic compounds.[1] They are shown to have antibacterial, antifungoid[2] and antimicrobial[3] properties. Studies indicate that dioximes are also reactive and take part in reactions such as synthesis of dinitrileoxides,[5] diamines, diamonium salts,[6] polymerisation[7] and formation of dicholorodioximes.[8]

Several methods of synthesis of oximes are known.[9] One of the most widely used methods of preparation of monoximes is the direct reaction of hydroxylamine hydrochloride with carbonyl compounds. 1,3-Dicarbonyl compounds, however, do not react or require more drastic conditions.

Following our pursuit of finding more facile and eco-friendly procedures of group transformations, we applied dry media conditions to the preparation of mono and 1,3-dioximes.[10] The results are shown in Tables 1 and 2. The monoximes were formed in good yields; no exceptions were found under the reaction conditions. Aldoximes and ketoximes showed similar behaviour and no chemoselectivity was observed; the results also indicated a high degree of generality. Molecular sieve (3Å) catalysed the synthesis of oximes without the need for reflux or microwave irradiation.

Table 1 illustrates various reaction conditions under which acetylacetone (as a representative model) reacted with hydroxylamine hydrochloride. According to the results obtained from these reactions, the optimum conditions were found and were applied to other carbonyl starting materials. Tabulated results in Table 2 and 3 are those obtained under the optimum conditions.



Scheme 1

Table 2 shows the results obtained from the reaction of 1, 3-diketones with $NH_2OH.HCl$. One of the diketones used, entry (3), did not react and the other one, entry (2), gave isoxazole. Despite previous reports, diketones do react under these conditions; the reactions are fast and the yields are high. Reactions are shown in Scheme 1.

Other catalysts such as silica gel, alumina, BaO, CaCO3 and MgO were examined but with no success. Entry (5) in Table 1 shows the optimum conditions for the preparation of

Table 1 Reaction of acetylacetone with $NH_2OH.HCl$

Entry	Condition					Yields/% dioxime
	Catalyst	$NH_2OH.HCl$	Solvent	Base	Time/min	
1	Mol. sieve	2.5 mmol	–	–	120	0
2	Mol. sieve	2.5 mmol	CHCl3 EtOH(abs)	–	120	0
3	Mol. sieve	2.5 mmol	–	$NaHCO_3$ NaOH AcONa Pyridine	120	0
4	Mol. sieve	2.5 mmol	$CHCl_3$	$NaHCO_3$ NaOH AcONa Pyridine	120	0
5	Mol. sieve	2.5 mmol	EtOH(abs)	$NaHCO_3$	25	70
				NaOH	20	84
				AcONa	15	92
				Pyridine	20	60
6	–	2.5 mmol	EtOH(abs)	$NaHCO_3$	120	50
				NaOH	120	65
				AcONa	120	70
				Pyridine	60	53

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Table 2 Reactions of 1,3-diketones with $NH_2OH.HCl$

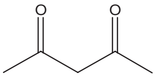
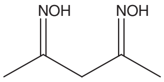
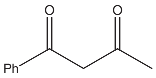
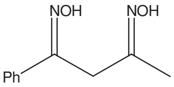
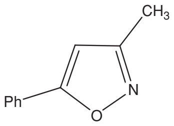
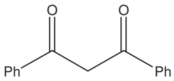
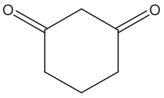
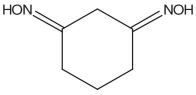
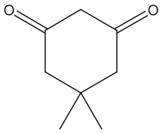
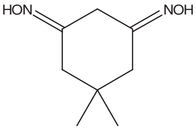
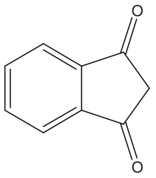
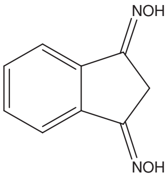
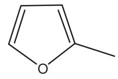
	1,3-Diketones	Product	Time/min	Yield/%
1			15	82
2			15	20
			15	60
3		No product	60	0
4			15	80
5			10	84
6			15	94

Table 3 Reactions of aldehyde or ketone with $NH_2OH.HCl$

Entry	Aldehyde or ketone		Time/min	Yield/%
	R_1	R_2		
1	Ph-	H	10	90
2	4-Cl-Ph-	H	15	94
3	4-Br-Ph-	H	15	93
4	4-NO2-Ph-	H	15	95
5	4-MeO-Ph-	H	15	80
6	4-(Me)2N-Ph-	H	15	94
7	4-Me-Ph-	H	15	96
8	2-NO2-Ph-	H	10	96
9	2-Me-Ph-	H	10	90
10	2-Cl-Ph-	H	15	95
11	3-Cl-Ph-	H	20	94
12	3-NO2-Ph-	H	15	94
13	3,4-di MeO-Ph-	H	20	95
14	Ph	CH3	20	90
15	Ph	Et	20	89
16	4-Cl-Ph-	CH3	15	89
17	4-Br-Ph-	CH3	20	90
18	4-Me-Ph-	CH3	20	87
19	Ph-	Ph-	20	85
20		H	15	89

oximes and dioximes. Entry (6) indicates that longer periods tend to decrease yields probably due to further reaction. The results obtained from the present method show several advantages over the previously reported ones. The reactions are carried out at room temperature, no need for heat or reflux. High yields are obtained without microwave assistance. Finally, 1,3-dioximes are formed under our conditions without the need for more drastic conditions.

Experimental

The purity of the compounds was checked by TLC over silica gel (CHCl3 as an eluent). The products were identified by melting point and IR. Spectra were run as KBr pellets using a Perkin-Elmer 843 IR spectrometer. NMR data were obtained using Bruker Avance 300 and 500 MHz spectrometers. MS spectra were recorded using a Shimadzu C/ 1100 Ex. spectrophotometer.

General method: Molecular sieve (2.50 g) was ground in mortar until powdered. Hydroxylamine hydrochloride (25 mmol, 1.72 g), aldehyde or ketone or 1,3-dicarbonyl compound (10 mmol) and anhydrous sodium acetate (25 mmol, 2.05 g) were mixed with powdered molecular sieve. The mixture was homogenised and wetted with absolute ethanol (10 ml) and grinding was continued for 15 more minutes until a sticky paste was formed. The reaction was stopped; the mixture was extracted with $CHCl_3$ (2×10 ml), the solvent was evaporated under reduced pressure which gave crystals that when washed with water and dried gave the corresponding oxime in high yields.

2,4-Pantanedionedioxime (**1**): White powder; m.p. 126 °C; IR (ν_{max} /cm^{-1}) (KBr): 980, 1630, 2800, 3400; ^{1}H NMR (DMSO): δ 1.7;(6H, S), 2.9 (2H, S), 3.4 and 11.0 (2H, S); ^{13}C NMR (DMSO): δ 13, 42, 153; Mass (*m/z*, %): 132.

1-phenyl-1,3-butanedionedioxime (**2a**): White powder, m.p. 140 °C; IR (ν_{max} / cm^{-1} (KBr): 980, 1630, 2800, 3400; ^{1}H NMR (DMSO): δ 1.6 (3H, S), 2.9 (2H, S), 3.4 and 11.0 (2H, S), 7.2–7.5 (5H, M); ^{13}C NMR (DMSO): δ 14, 44, 153, 155, 128, 129, 131, 144; Mass (*m/z*, %): 194.

3-Methyl-5-phenylisoxazole (**2b**): Exactly agree with ref. 11 a white powder, m.p. 67 °C; IR (ν_{max} / cm^{-1}) (KBr) 790, 1620, 2850, 3100; ^{1}H NMR (DMSO): δ 2.32 (3H, S), 6.85 (1H, S), 7.50–7.84 (5H, M); ^{13}C NMR (DMSO): δ 11, 101, 125, 127, 129, 160, 168; Mass (*m/z*, %): 161.

1,3-Cyclohexandionedioxime (**3**)**:** White powder, m.p. 135–139 °C; IR (ν_{max}/ cm^{-1} KBr: 980, 1650, 2810, 3400; ^{1}H NMR (DMSO): δ 1.7 (2H, M), 2.13 (4H, M), 3.4 (2H, S), 3.5 and 10.3 (2H, S); ^{13}C NMR (DMSO): δ 27, 32, 44, 153; Mass (*m/z*): 142.

5,5-Dimethyl-1,3-cyclohexandionedioxime (**4**)**:** White yellowish powder; m.p. 169–170°C; IR (ν_{max}/ cm^{-1}) KBr: 980, 1650, 2815–2900, 2350–3500; ^{1}H NMR (DMSO): δ 0.86 (6H, S), 2.14 (4H, S), 3.42 (2H, S), 3.5 and 10.3 (2H, S); ^{13}C NMR (DMSO): 24, 28, 32, 44, 153; Mass (*m/z*): 170.

1,3-Indandionedioxime (**5**)**:** Yellow powder; m.p.: >200 °C, IR (ν_{max}/ cm^{-1}) KBr: 970, 1640, 2810, 2900, 2330–3510; ^{1}H NMR (DMSO): δ 3.4 (2H, S), 3.5 and 11.3 (2H, S), 7.4 (2H, D), 7.6 (2H, D); ^{13}C NMR (DMSO): 29, 121, 131, 139, 153; Mass (*m/z*): 176.

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