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$NH_2OH.HCl/BaCl_2$: A Convenient System for Synthesis of Oximes from the Corresponding of Organic Carbonyl Compounds

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ABSTRACT

A variety of aldehydes and ketones were converted to their corresponding oximes $NH_2OH{\cdot}HCl/BaCl_2$ system in reflux conditions.

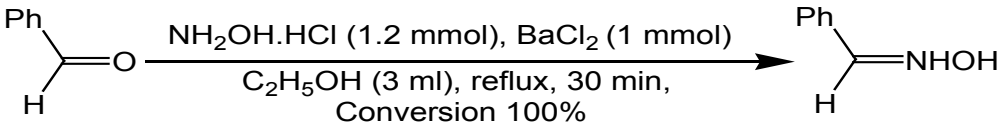
Keywords: Oximes, aldoximes, acetophenone oximes, $H_2NOH.HCl$, $BaCl_2$.

INTRODUCTION

Oximes have many applications in organic synthesis[1]. These compounds have antimicrobial, antioxidant, antitumor, anti-depressive, antiviral agents, and anticonvulsant properties[2-7]. Some oximation methods have been reported[8]. However our ongoing attentions to the development of new modified methods in organic synthesis[8-15], we have investigated the oximation of a variety of carbonyl compounds with $NH_2OH{\cdot}HCl$ in the presence of $BaCl_2$.

RESULTS AND DISCUSSIONS

For finding optimization reaction conditions bezaldehyde and acetophenone have been used as model compounds. Experiments showed that using $NH_2OH.HCl$ (1.2 mmol) and $BaCl_2$ (1 mmol) in C_2H_5OH (3 ml) was the best conditions for the oximation of benzaldehyde. The reaction was completed within 30 minutes in reflux conditions with the excellent yield (95%) of the product as shown in scheme 1.



Scheme 1:

Table 1: Oximation of Aldehydes (1 mmol) by $NH_2OH.HCl$ (1.2 mmol)/$BaCl_2$ (1 mmol) Under Reflux Conditions in Ethanol (3 mL)

Entry	Substrate	Product	^{1}H chemical shift of C(H) =N(δ ppm)	Time(min) Yield(%)[a]	^{1}HNMR(δ ppm), IR (cm^{-1}) and m.p. (°C)[7]	
1	benzaldehyde	(*Z*)-benzaldehyde oxime	8.18	30, 95	^{1}HNMR ($CDCl_3$)	7.41–7.59 (m, 5H, Ar), 8.01 (bs, 1H, OH), 8.18 (s, 1H, CH).
					IR (liquid film)	3308 (NOH), 1694, 1497, 1450, 1294, 1073, 958, 756, 691.
					m.p.	-
2	4-bromobenzaldehyde	(*Z*)-4- benzaldehyde oxime	8.10	35, 95	^{1}HNMR ($CDCl_3$)	5.12 (bs, 1H, OH), 7.27-7.55 (m, 4H, Ar), 8.10 (1H, CH).
					IR (KBr)	3367 (NOH), 1701, 1589, 1489, 1365, 1067, 968, 703.
					m.p.	110-112
3[b]	N,N-dimethylbenzaldehyde	(*Z*)- N, N-dimethyl benzaldehyde oxime	8.07	40, 96	^{1}HNMR ($CDCl_3$)	3.01 (s, 6H, CH_3), 5.31 (s, 1H, OH), 6.69 (d, 2H, Ar), 7.46 (d, 2H, Ar), 8.07 (s, 1H, CH).
					IR (KBr)	3237 (NOH), 1611, 1447, 1100, 811, 736.
					m.p.	143-145
4[b]	4-methylbenzaldehyde	(*Z*)-4-methyl benzaldehyde oxime	8.15	40, 93	^{1}HNMR ($CDCl_3$)	2.38 (s, 3H,CH_3), 7.21 (d + bs, 3H, Ar + OH), 7.49 (d, 2H, Ar), 8.15 (s, 1H, CH).
					IR (KBr)	3400 (NOH), 1635, 1409, 1265, 1040, 896, 740.
					m.p.	80-81
5[b]	3-methylbenzaldehyde	(*Z*)-3-methyl benzaldehyde oxime	8.15	40, 92	^{1}HNMR ($CDCl_3$)	2.38 (s, 3H,CH3), 7.21-7.41 (m, 4H, Ar), 7.82 (bs, 1H, OH), 8.15 (s, 1H, CH).
					IR (liquid film)	3314 (NOH), 1632, 1584, 1489, 1410, 1309, 1266, 954, 786..
					m.p.	-
6	4-nitrobenzaldehyde	(*Z*)-4-nitrobenzaldehyde oxime	8.27	30, 93	^{1}HNMR ($CDCl_3$)	7.76(d, 2H, Ar), 8.23 (d + bs, 3H, Ar + OH), 8.27 (s, 1H, CH).
					IR (KBr)	3077 (NOH), 1603, 1535, 1348, 1108, 970, 847, 748, 686.

				m.p.	129-130
7[b]	2-methoxylbenzaldehyde	(*Z*)-2-methoxy benzaldehyde oxime	8.49	^{1}HNMR ($CDCl_3$)	3.89 (s, 3H,OCH_3), 5.97, (bs, 1H, OH), 6.97 (q, 2H, Ar), 7.38 (t, 1H, Ar), 7.68 (d, 1H, Ar), 8.49 (s, 1H, CH).
				IR (KBr)	3304 (NOH), 1632, 1497, 1449, 1299, 1211, 957, 870, 756, 692.
				m.p.	75-77
8[b]	4-methoxybenzaldehyde	(*Z*)-4-methoxy benzaldehyde oxime	8.11	^{1}HNMR ($CDCl_3$)	3.84 (s, 3H,OCH_3), 6.92 (d, 2H, Ar), 7.53 (d + bs, 3H, Ar + OH), 8.11 (s, 1H, CH).
				IR (KBr)	3312 (NOH), 1606, 1514, 1254, 1175, 956,832, 835.
				m.p.	43-44

[a]Yields refer to isolated pure products (±2%).

A variety of aldehydes were ground with $NH_2OH{\cdot}HCl/BaCl_2$ system under optimized reaction conditions. In this approach, the corresponding *Z*-aldoximes were obtained in quantitative yield (93-98%). The results have been reported in table 1. Then, the oximation of ketones was also performed well by $NH_2OH{\cdot}HCl/BaCl_2$ system. Experiments showed the oximation of ketones requires higher molar amounts of NH2OH·HCl (1.5 mmol) and $BaCl_2$ (1 mmol) *vs.* 1 mmol of the substrates. The reaction of acetophenone was completed in 65 minutes with the excellent yield (93%) as shown in scheme 2.

A variety of acetophenones were ground with $NH_2OH{\cdot}HCl/BaCl_2$ system under optimized reaction conditions. In this approach, the corresponding *E*-acetophenonoximes were obtained in quantitative yield (87-95%). The results have been reported in table 2.

All substrates and reagents were purchased from commercially sources with the best quality. IR and ^{1}H NMR spectra were recorded on PerkinElmer FT-IR RXI and 300 MHz Bruker spectrometers, respectively. The products were characterized by their ^{1}H NMR or IR spectra and comparison with authentic samples (melting points). All yields referred to isolated pure products. The purity of products was determined by TLC and ^{1}H NMR. Also, reactions were monitored by TLCs utilizing plates cut from silica gel 60 F_{254} aluminum sheets.

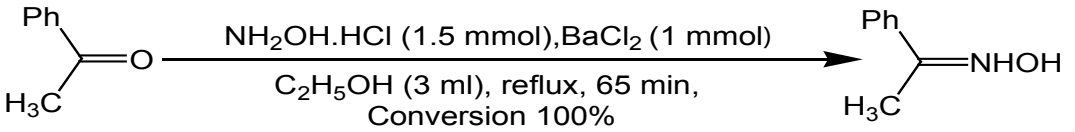
A typical procedure for the oximation with $NH_2OH{\cdot}HCl/BaCl_2$ system

In a round-bottomed flask (10 mL) equipped with a condenser, a mixture of benzaldehyde (0.106 g, 1 mmol), $NH_2OH{\cdot}HCl$ (0.084 g, 1.2 mmol) and $BaCl_2$ (0.2 g, 1 mmol) in ethanol (3 mL) was prepared. The mixture was stirred under reflux conditions for 30 min. The progress of the reaction was monitored by TLC. After completion of the reaction, H_2O (10 mL) was added and the reaction mixture was continued to stirring for 5 min. The product has been extracted with CH_2Cl_2 (3õ15 mL).The mixture was dried over anhydrous Na_2SO_4. Evaporation of the solvent and a short column chromatography of the resulting crude material over silica gel (eluent; CCl_4/Et_2O: 5/2) afforded the pure benzaldoxime (0.115 g, 95 % yield, table 1, entry 1).

Table 2: Oximation of Ketones (1 mmol) by $NH_2OH.HCl$ (1.5 mmol)/$BaCl_2$ (1 mmol) Under Reflux Conditions in Ethanol (3 mL)

Entry	Substrate	Product	^{1}H chemical shift of CH_3 (δ ppm)	Time(Sec) Yield (%)[a]	^{1}HNMR (δ ppm), IR (cm^{-1}) and m.p.(°C)[7]	
1	acetophenone	(*E*)-acetophenone oxime	2.34	65, 93	^{1}HNMR ($CDCl_3$)	2.34 (s, 3H, CH_3), 7.40–7.63 (m, 5H, Ar), 8.10 (s, 1H, OH).
					IR (KBr)	3305 (NOH), 1630, 1602,1498, 1446, 1261, 1096, 925, 757, 695.
					m.p.	54-55
2	4-methylacetophenone	(*E*)-4-methylacetophenone oxime	2.38	70, 87	^{1}HNMR ($CDCl_3$)	2.31 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 6.35 (s, 1H, OH), 7.21 (d , 2H, Ar), 7.54 (d, 2H, Ar).
					IR (KBr)	3397 (NH), 1636, 1420, 1265, 1095, 817, 739.
					m.p.	80-81
3	4-methoxyacetophenone	(*E*)-4-ethoxyacetophenone oxime	2.30	100, 90	^{1}HNMR ($CDCl_3$)	2.3 (s, 3H, CH_3), 3.83 (s, 3H, OCH_3), 6.91 (d + bs, 3H, Ar + OH), 7.58 (d, 2H, Ar).
					IR (KBr)	3305 (NOH), 1602, 1446, 1216, 1096, 925, 757.
					m.p.	79-80
4	benzalacetone	(*E*)-benzalacetone oxime	2.18	70, 95	^{1}HNMR ($CDCl_3$)	7.28(Ar, 2H), 6.87(Ar, 2H), 4.81 (CH, 1H), 3.78(OCH_3, 3H), 2.53 (OH, 1H), 1.45 (CH_3, 3H).
					IR (KBr)	3271 (NOH), 1633, 1448, 1260, 1029, 964, 802, 1034, 749, 691.
					m.p.	111-113

[a]Yields refer to isolated pure products (±2%).



Scheme 2:

CONCLUSION

The oximation of a variety of aldehydes and ketones was carried out efficiently with $NH_2OH{\cdot}HCl/BaCl_2$ system. The reactions were performed in ethanol under reflux conditions. Excellent yields (93-98%) of products in appropriate times (30-100 min) have been achievement.

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