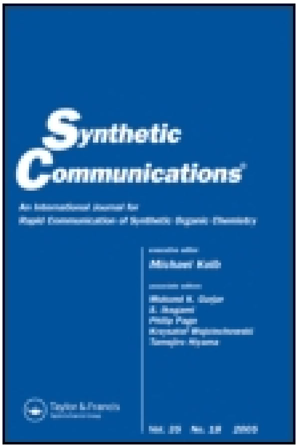


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

A Facile Beckmann Rearrangement of Oximes with $AlCl_3$ in the Solid State

M. Ghiaci [a] & G. Hassan Imanzadeh [a]

[a] Department of Chemistry, Isfahan University of Technology, Isfahan, 84156, Iran

To cite this article: M. Ghiaci & G. Hassan Imanzadeh (1998): A Facile Beckmann Rearrangement of Oximes with $AlCl_3$ in the Solid State, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 28:12, 2275-2280

To link to this article: http://dx.doi.org/10.1080/00397919808007044

SYNTHETIC COMMUNICATIONS, 28(12), 2275–2280 (1998)

A Facile Beckmann Rearrangement of Oximes with $AlCl_3$ in the Solid State

M. Ghiaci* and G. Hassan Imanzadeh

Department of Chemistry
Isfahan University of Technology
Isfahan,84156,Iran

A facile and efficient synthetic procedure, for Beckmann rearrangement of oximes with $AlCl_3$ in the absence of solvent is developed. We have been able to convert cyclohexanone oxime to ε-caprolactam in a quantitative yield.

Many reagents have been used in the Beckmann rearrangement of ketoximes. When oximes are treated with PCl_5[1] or a number of other reagents, they rearrange to substituted amides[2]. Among other reagents used have been concentrated H_2SO_4, formic acid[3], liquid SO_2, HMPA[4], $SOCl_2$[5], silica gel[6], P_2O_5 -methane sulfonic acid[7], HCl-HOAc, Ac_2O[8], polyphosphoric acid[9]. In connection with our interest in solid-state reactions, the use of $AlCl_3$ for these rearrangement was examined and it was found that $AlCl_3$ react with various types of ketoximes under mild conditions to give the corresponding amide in one step, and in a quantitative yield.

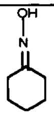
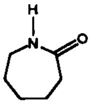
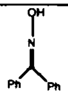
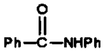
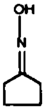
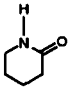
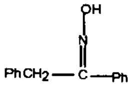
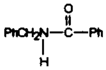
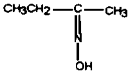
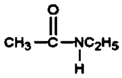
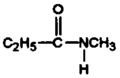
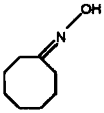
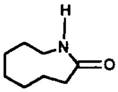
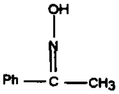
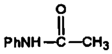
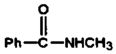
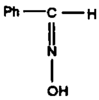
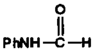
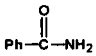
Here we would like to report the novel utility of aluminium chloride as an efficient reagent for conversion of ketoximes to amides in the solid state.

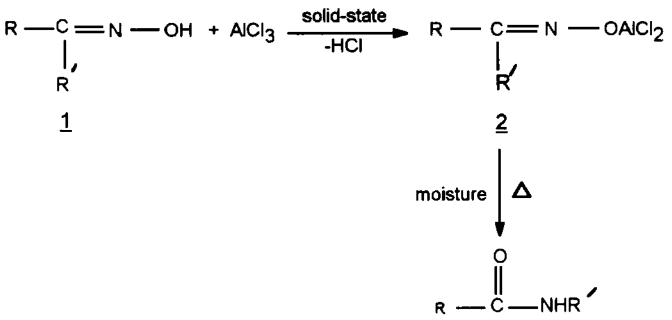
In an attempt to examine the Lewis acid property of $AlCl_3$ in the solid state, cyclohexanone oxime was mixed with $AlCl_3$ in a ratio of 1: 3 respectively in an agate mortor, at room temperature, an exothermic reaction ensued instantaneously giving HCl vaper and a molten mass. Working up a small amount of the mass simply by adding cold water and ether and monitoring the reaction mixture by TLC showed two spots in approximately 50:50 ratio of the oxime and a new spot that was characterised as the corresponding lactam. By heating the reaction mixture at 60-80°C for 30 min, the reaction was completed quantitatively.

Adopting the above method, various oximes have been isomerised to the corresponding amides and we find that in all ketoximes cases the yields are quantitative and the method is much better than all the methods known so far for its simplicity and high conversion.The list of ketoximes that have been isomerised by this method are given in Table1. This reaction is only useful for converting ketoximes to the corresponding amides and not applicable for the conversion of aldoximes. Thus, benzaldoxime when submitted to this isomerisation reaction, it was converted to a mixture of benzamide (20%) , N-Phenyl formamide (35%) and benzonitrile (trace). In the case of salicyl aldoxime we recovered the starting material .

The mechanism of this isomerisation is not clearly understood .The possibility of formation of an organoaluminium intermediate **2** is not ruled out because of the libration of HCl at once. In the second step, the conversion should take place by the migration of one of the alkyl or aryl groups. The group that migrates is generally the

Table 1. Rearrangement of ketoximes to the corresponding amides.

Entry	Substances	AlCl₃ :Oxime mole	Temp. (° C)	Products	Yields based on NMR & TLC
1		2:1	50-80		%100
2		4:1	70	 $Ph{-}C(=O){-}NHPh$	%100
3		3:1	40		%100
4	 $PhCH_2{-}C(=N{-}OH){-}Ph$	3:1	35-40	 $PhCH_2N(H){-}C(=O){-}Ph$	%100
5	 $CH_3CH_2{-}C(=N{-}OH){-}CH_3$	2:1	50-70	A:  $CH_3{-}C(=O){-}N(H)C_2H_5$ B:  $C_2H_5{-}C(=O){-}N(H)CH_3$	A:B (%100) 2:1
6		2:1	50		%100
7	 $Ph{-}C(=N{-}OH){-}CH_3$	3:1	70-80	A:  $PhNH{-}C(=O){-}CH_3$ B:  $Ph{-}C(=O){-}NHCH_3$	A:B (%100) 4:1
8	 $Ph{-}C(=N{-}OH){-}H$	3:1	50	A:  $PhNH{-}C(=O){-}H$ B:  $Ph{-}C(=O){-}NH_2$ C: $Ph{-}C{\equiv}N$	mixture of products (%40)



one anti to the leaving group, and this is often used as a method of determining the configuration of the oxime. However it is unequivocal[10]. It is known that with some oximes the syn group migrates and that with others, especially where R and R′ are both alkyl, mixture of the two possible amides are obtained. For example, in the case of ethyl methyl ketoxime (entry 5), a mixture of the two possible amides are obtained. In the entry 4, we have only seen the migration of benzyl group, but in the case of methyl phenyl ketoxime, it is the aryl group that preferentially migrates.

Solvents were used directly as obtained from the supplies. Reagents were employed as purchased from Aldrich or Merck. Thin layer chromatography (TLC) was carried out using glass sheets precoated with sillica gel 60F. Melting points were determined on an Electrothermal Galler Kamp apparatus and uncorrectly. ^{1}HNMR spectra were recorded on a Varian EM-390(60 MHz). IR spectra were obtained using a Shimatzo IR-435 spectrometer. The products ratio and purity of the products were determined by GC and ^{1}H spectroscopy, and comparing with euthentic samples.

Isomerizasion of oximes to amides.

General procedure.- A mixture of ketoxime , and anhydrous $AlCl_3$ was throughly ground in an agate motor for a few minutes. Hydrogen chloride was evolved violently.

The molten mass was ground by heating (40-80°C) for 30 min. The reaction mixture was mixed with crushed-ice and extracted with $CHCl_3$. The chloroform solution was dried over $MgSO_4$. The solvent was removed in vaccuo to give the product.

ε-Caprolactam.-A mixture of cyclohexanone oxime (1.4 g, 12.4 mmol) and anhydrous aluminium chloride (2.4 g, 26 mmol) was throughly ground in an agate motor for a few minutes. After the evolution of HCl, the reaction mixture was ground by heating (50-80°C) for 30 min. The reaction mixture was mixed with crushed ice and the product was extracted by a continuce extraction apparatus. Distillation of the residue at reduce pressure afforded ε-caprolactam. Isolated yield :1.35 gr(97%) m.p. 68-69°.

Acknowledgment. We thank the Isfahan university of technology for financial support of this research. We also thank Mr. A.Reza Modarresi for his primary participation in this work.

References

1. R.T conley and R.J lange, *J.Org.Chem*. ***1963**, 28, 210.*
2. For review see R.E. Gawley, *Org.React*. **1988,** 351-420; C.G. McCouty, in Patai The chemistry of the Carbon-Nitrogen Double Bond; *Wiley: New York, 1970, pp.408-439*
3. Tivan Es, *J.chem.Soc,* **1965**,*3881.*
4. R.S.Morson,B.M.Broline, *Can.J.Chem.* **1973**, *51, 942*; J.T. Gupton. , J. P. Idoux;R.,Leonard G., Decrescenzo, *Synth.Commun.* **1983** ,*13, 1083*
5. R.N. Butla and D.A. O' Donoghue , *J. Chem. Res. (5)* **1983**, *18.*
6. A. Costa, and R.Mestres,J.M. Riego, *Synth. Commun.* **1982** , *12, 1603*
7. P.E , Eaton ,G.R coulson ,J.T. Lea , *J. Org. Chem.* **1973**, *38, 4071*
8. R.F. Broun, N. M. van Gulick , and G.H.Schmid, *J. Amer. Chem. Soc.77 , 1094 (1955).*

9. For a review of Beckmann rearrangements with polyphosphoric acid, see A.L.Beckwith , in *J. Zabicky, Ref.230, pp. 131-137. Co. P. T. Lansbury* , *M. R.. Mancuso;*

10. P. T. Lansbury, N. R. Mancuso, *Tetrahedron Lett.* **1965**, *2445*

(Received in The Netherlands 21 November 1997)