This article was downloaded by: [Selcuk Universitesi] On: 19 December 2014, At: 20:29 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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/Isyc20

# Beckmann Rearrangement of Substituted Diaryl Ketoximes Using Fecl<sub>3</sub> Impregnated Montmorillonite K10

S. G. Pai<sup>a</sup>, A. R. Bajpai<sup>a</sup>, A. B. Deshpande<sup>a</sup> & S. D. Samant<sup>a</sup>

<sup>a</sup> Organic Chemistry Research Laboratory, Bombay University, Department of Chemical Technology, Matunga, Bombay, 400 019, India Published online: 22 Aug 2006.

To cite this article: S. G. Pai, A. R. Bajpai, A. B. Deshpande & S. D. Samant (1997) Beckmann Rearrangement of Substituted Diaryl Ketoximes Using Fecl<sub>3</sub> Impregnated Montmorillonite K10, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 27:3, 379-384, DOI: <u>10.1080/00397919708006036</u>

To link to this article: http://dx.doi.org/10.1080/00397919708006036

## PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at <a href="http://www.tandfonline.com/page/terms-and-conditions">http://www.tandfonline.com/page/terms-and-conditions</a>

## BECKMANN REARRANGEMENT OF SUBSTITUTED DIARYL KETOXIMES USING FeCl<sub>3</sub> IMPREGNATED MONTMORILLONITE K10

S.G. Pai, A.R. Bajpai, A.B. Deshpande, and S.D. Samant\*.

Organic Chemistry Research Laboratory, Bombay University Department of Chemical Technology, Matunga, Bombay - 400 019, India

**ABSTRACT**: Montmorillonite K10 was impregnated with FeCl<sub>3</sub> in acetonitrile. The catalyst was found to catalyze the Beckmann rearrangement of substituted diaryl ketoximes significantly, giving selectively *anti* migration.

The Beckmann rearrangement has been of tremendous interest to all practicing organic chemists, as the reaction effects a nitrogen insertion into a carbon framework<sup>1,2</sup>. It generally proceeds through *anti* migration. The conventional Beckmann rearrangement usually requires the use of excess amounts of strong Bronsted acids such as conc.  $H_2SO_4$  or polyphosphoric acid, which cause serious problems, such as product decomposition and formation of a large amount of inorganic salts caused by neutralization. To circumvent these problems, during recent years, different solid catalysts such as metal oxides<sup>3</sup>, metal phosphates<sup>4</sup>, supported boria<sup>5</sup>, zeolites<sup>6</sup>, aluminosilicates<sup>7</sup>, including clays<sup>8,9,10</sup> and pillared clays<sup>11</sup> are being used. However, most of these reactions are vapor phase reactions

<sup>\*</sup>To whom correspondence should be addressed

or are carried out at very high temperatures (>523 K); or when carried out in the solvent phase are generally sluggish. For example, Tonsil day rearranged only activated p-OH/OCH, Acetophenone oximes, while it led to the hydrolysis product i.e. the ketone in all the other cases<sup>10</sup>. Benzanilide was obtained from Benzophenone oxime in 75% yield using Montmorillonite KSF, after prolonged reflux in toluene<sup>10</sup>. There is only one report on the Beckmann rearrangement using cation-exchanged acidic clays, i.e. Al<sup>3+</sup>-Montmorillonite<sup>11</sup>.

Since Laszlo's pioneering work on cation exchanged clays in Friedel-Crafts alkylations<sup>12</sup> and acylation<sup>13</sup>, these clays have been extensively used in acid catalyzed reactions. It has been found that  $Fe^{3+}$ -exchanged Montmorillonite K10 conspicuously singles out among the cation exchanged clays in catalyzing Friedel-Crafts reaction. This prompted us to use a similar catalyst to catalyze the Beckmann Rearrangement of diaryl ketoximes. It has also been observed that ZnCl<sub>2</sub> impregnated Montmorillonite K10 (clayzic) was a better catalyst than Zn<sup>2+</sup> exchanged Montmorillonite K10<sup>14</sup>. This is believed to be due to faster diffusion of the reactants onto the catalytic sites, which lead to a much improved catalytic activity<sup>15</sup>.

Inspired by this, we prepared FeCl<sub>3</sub> impregnated Montmorillonite K10 (FeCl<sub>3</sub>- Mont K10) using acetonitrile as a solvent for Beckmann rearrangement, where unusually high catalytic activity coupled with high stereospecificity was noted. In order to have a background knowledge of the activity of unimpregnated clays (ion-exchanged, acid treated and pillared clays), the oxime 1a was rearranged to the anilide 2a using different clays (Table 1). All the reactions were carried out in toluene, at its reflux temperature in the presence of the catalyst. Using 1a, the amount of catalyst was optimized and an oxime to clay ratio of 1 : 2.5 was taken. Toluene was found to be the best solvent amongst all the solvents tried and the best yields were obtained in boiling toluene. The important observation was that a

Entry	Clay Catalyst		Yield (%)	•
		1a	2a	<b>4</b> a
1.	Na <sup>+</sup> - Montmorillonite <sup>b</sup>	67	13	20
2.	Montmorillonite KSF	85	11	4
3.	Montmorillonite K10	42	56	2
4.	Al-PILC°	66	32	1

Table 1: Beckmann Rearrangement of 1a using various clay catalysts.

<sup>a</sup>: The yields are based on GC analysis (error of ± 4%) and are compared with known weight of the standard. Yields are calculated after 5 minutes of reflux in Toluene. Clays were dried at 120°C for 2 h prior to use.
 <sup>b</sup>: Natural Na<sup>+</sup>-exchanged Montmorillonite (pH = 7) procured from Sud-Chemie AG, Munich, Germany.
 <sup>c</sup>: Gift sample Al-PILC (EX 534) procured from Sud-Chemie AG Munich, Germany.

large amount of 1a remained unreacted. Particularly striking was the poor activity of highly Bronsted acidic Montmorillonite KSF<sup>16</sup>.

Subsequently, the reaction of various benzophenone oximes (1a -1i) were carried out using the FeCl<sub>3</sub>-Mont K10 catalyst (Scheme 1, Table 2). The important observation was that in no case the oxime underwent hydrolysis/ fragmentation and the conversion was complete in 5-12 minutes. This observation was novel on the background of various side reactions usually accompanying Beckmann rearrangement<sup>2</sup>.



Entry	Reactant	$\mathbf{R}^1$	R <sup>2</sup>	Reaction	Combined	Product <sup>e</sup>	
	1			time	yield⁵	yield (%)	
				(minutes)	of 2 & 3	2	3
1	a	Н	Н	5	98	100	-
2	b	OCH <sub>3</sub>	OCH <sub>3</sub>	5	93	100	-
3	c	CH <sub>3</sub>	CH3	5	91	100	-
4	d	<b>C</b> 1	C1	8	97	100	-
5	e	F	F	10	92	100	-
6	f	CH,	Н	5	<b>9</b> 7	49	51
7.	g	OCH <sub>3</sub>	Н	5	95	46	54
8.	h	C1	Н	10	94	41	59
9.	i	Br	Н	12	98	36	64

 Table 2 :\* Beckmann rearrangement of various substituted diaryl ketoximes using

 FeCL-Mont K10

<sup>a</sup>: The two anilides formed in each case (1f-1i) (*anti* - migration of both the syn - and the *anti* - isomer ) were confirmed using a GC- MS. <sup>b</sup> : represents the total amount of 2 & 3 isolated. <sup>c</sup> : Determined from <sup>1</sup>H-NMR measurements

Also, the catalyst can be recovered and reused for upto 5 cycles (after activation for 1 h at 280°C) without any significant loss in activity. The Beckmann rearrangement is generally suggested to proceed through *anti* migration, the *syn*-and the *anti*- forms of 1f-1i are expected to give the corresponding anilides 2 and 3 respectively. FeCl<sub>3</sub>-Mont K10 directed the reaction through stereospecific *anti* migration. Thus, in the case of 1f-1i, the relative ratio of 2:3 was almost in consonance with the reported ratios<sup>17</sup>.

### Experimental :

Melting points were determined on a Veego Precision M.P. apparatus and are uncorrected. IR spectra were recorded on a Jasco FTIR 300E spectrometer. <sup>1</sup>H-NMR were recorded on a 300 MHz (Varian VXR 300S) in DMSO-d<sub>x</sub>. GC-MS are recorded on a Hewlett Packard GCD Series Gas Chromatograph equipped with an ECD. G.C. analysis were carried out on a Chemito 2865 Gas Chromatograph using a 5% SE-30 column. Ketoximes were prepared according to the literature method<sup>18</sup>.

Catalyst Preparation : FeCl<sub>3</sub> (15g) was dissolved in dry acetonitrile (60 ml) and Montmorillonite K10 (10g) was added over a period of 10 min. The resulting slurry was stirred at room temperature for 5 h. The clay was then filtered, washed with dry acetonitrile (10 ml), and then with dry benzene (3 X 20 ml). The yellowish powder obtained was activated in air at 280°C for 5 h, when a reddish powder was obtained. The clay was then stored in a vacuum desiccator. It was activated for 2 hours at 120°C prior to use. It is designated as FeCL- Mont K10.

**Beckmann Rearrangement** (General Procedure) : A mixture of the ketoximes (0.4g) and FeCl<sub>3</sub>- Mont K10 (1 g) (or any other clay as is specified in Table 1) was stirred in toluene at its reflux temperature. The reaction was monitored by TLC. The mixture was cooled and filtered. The clay residue was extracted with boiling acetone and the extract was combined with the toluene filterate. The solvent was vacuum distilled to yield the anilide which was recrystallized from a suitable solvent or purified by column chromatography (Ethyl Acetate - Hexane).

Acknowledgement : The authors are grateful to the Indo-French Centre for the Promotion of Advanced Research (Project no.1106-2) for financial assistance, to the Regional Sophisticated Instrumentation Centre, IIT, Bombay for providing the NMR and the Mass spectra and to SUD-CHEMIE AG, Munich, for providing some free clay samples.

#### References:

- 1. Gawley, R.E., Org. React., 1988, 35, 1.
- 2. Donaruma, L.G. and Heldt, W.Z., Org. React., 1960, 11, 1.

- Yashima, T., Horie, S., Saito, S. and Hara, N., *Nippon Kagaku Kaishi*, 1977, *J*, 77. (C.A.- 86: 90264s)
   a) Costa, A., Deya, P.M., Sinisterra, J.V and Marinas, J.M., *Can. J. Chem.*, 1980, 58, 1266. b) Costa,
   A., Deya, P.M., Sinisterra, J.V and Marinas, J.M. *An. Quim.*, *Ser. C.*, 1982, 78, 43. (C.A.- 97: 55025v)
   a) Sato, S., Hasebe, S., Sakurai, H., Urabe, K. and Izumi, Y., *Appl. Catal.*, 1987, 29, 107. b) Sato,
   S., Urabe, K. and Izumi, Y., *J. Catal.*, 1986, 102, 99.
   a) Yashima, T., Minra, K. and Komatsu, T., *Stud. Surf. Sci. Catal. (Zeolites and Related Microporous*)
- Materials, Pt. C), 1994, 84, 1897. b) Aucejo, A., Burguet, M.C., Corma, A. and Fornes, V., Appl. Catal., 1986, 22, 187. c) Reddy, J.S., Ravishankar, R., Sivasanker, S. and Ratnasamy, R.Catal. Lett., 1993, 17, 139. d) Landis, P.S. and Venuto, P.B. J. Catal., 1966, 6, 245 e) Bhawal, B.M., Mayabhate, S.P., Likhite, A.P. and Deshmukh, A.R.A.S., Synth. Commun., 1995, 25, 3315.
- 7. Murakami, Y., Saeki, Y. and Ito, K., Nippon Kagaku Kaishi, 1978, 1, 21. (C.A. 88: 89178b)
- 8. a) Gutierrez, E., and Ruiz-Hitzky, E., Pillared Layered Struct.: Current Trends and Applications, Mitchell, I.V. (Ed.), Elsevier Appl.Sci., London, 1990, pp.199-208.
- 9. Alvarez, C., Cano, A.C., Rivera, V. and Marquez, C., Synth. Commun. 1987, 17, 279.
- 10. Meshram, H.M., Synth. Commun., 1990, 20, 3253.
- 11. Gutierrez, E., Aznar, A.J. and Ruiz-Hitzky, E., Stud. Surf. Sci. Catal. (Het. Catalysis and Fine Chemicals II), 1991, Elsevier, Amsterdam, pp. 539-547.
- 12. Laszlo, P. and Mathy, A., Helv. Chim. Acta., 1987, 70, 577.
- 13. Cornelis, A., Gerstmans, A., Laszlo, P., Mathy, A. and Zieba, I, Catal. Lett., 1990, 6, 103.
- 14. Clark, J.H., Kybett, A.P., Macquarrie, D.J., Barlow, S.J. and Landon, P. J. Chem.Soc., Chem. Commun., 1989, 1353.
- 15. Laszlo, P., Surfactant Sci. Ser. (Kinet. Catal. Microheterogeneous Syst.), Gratzel, M. and Kalyanasundaram, K. (Eds.) Marcel-Dekker, New York, 1991, 38, pp. 437-59.
- 16. Cseri, T., Bekassy, S., Figueras, F., Cseke, E., de Menorval L.C. and Dutarte, R., Appl. Catal.-A: Gen. 1995, 99, 1.
- 17. Bachmann, W.E. and Barton, I.H.M., J.Org. Chem., 1938, 3, 300.
- Vogel, A.I., "Textbook of Practical Organic Chemistry", 5th ed., ELBS and Longmann, 1989, 1049.

(Received in the UK 6th June 1996)