Catalysis Communications 54 (2014) 11–16

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Self-catalyzed direct amidation of ketones: A sustainable procedure for acetaminophen synthesis

Elia Rancan [a,c], Fabio Aricò [b,c], Giuseppe Quartarone [a,c], Lucio Ronchin [a,c,*], Pietro Tundo [b,c], Andrea Vavasori [a,c]

[a] Department of Molecular Science and Nanosystems, Ca' Foscari University, 2137 Dorsoduro, 30123 Venice, Italy
[b] Department of Environmental Science, Informatics and Statistics, Ca' Foscari University, 2137 Dorsoduro, 30123 Venice, Italy
[c] Green Chemistry Group, 2137 Dorsoduro 30123 Venice, Italy

ARTICLE INFO

Article history:
Received 17 April 2014
Received in revised form 7 May 2014
Accepted 16 May 2014
Available online 25 May 2014

Keywords:
Acetaminophen
Amides
Self-catalyzed
Oxiamation
Beckmann rearrangement

ABSTRACT

High yielding amination of ketones and benzaldehyde in acid-less conditions has been conducted on several ketones to achieve amides and nitriles. The reactivity of the selected substrates showed to depend on both oxiamation and Beckmann rearrangement reaction rates. Oxiamation allows the in-situ production of hydrochloric acid that enables Beckmann rearrangement of the oxime to form the corresponding amide or nitrile. It is noteworthy that, using this one-pot synthetic approach, *N*-acetyl-4-aminophenol (acetaminophen drug), can be easily synthesized starting from 4-hydroxy-acetophenone in high yield. Acetanilide and ε-caprolactam can be also efficiently synthesized employing this synthetic procedure.

1. Introduction

Amides are building blocks and/or final product in a wide range of commodities, i.e., rubber, paper, varnish, in water treatment and in the synthesis of several pharmaceutical molecules [1–4]. A poignant example is acetaminophen (*N*-acetyl-4-aminophenol), the amide commercially known as acetaminophen, whose production is in continuous growth [4–6].

In the past, the aspects related to the sustainability (economical and environmental) inherent to the industrial production of amide have been poorly considered, on the contrary recently, the development of new processes to fulfill this requirement has become of great interest [5].

In many industrial processes amides are synthesized by a two-step reaction: oxiamation of the ketone, followed by Beckmann rearrangement [5–9]. The first step proceeds in the presence of a base, thus obtaining hydroxylamine as nucleophile, while the rearrangement is generally carried out in mineral acid [10–12]. Furthermore, neutralization typically with aqueous ammonia is required to recover the pure product [5,6]. A commodity already produced according to this synthetic approach is caprolactam the monomer of nylon [6] even though nowadays, the new plant is mainly based on the new sulfuric acid free processes (Scheme 1, Enichem–Sumitomo process) [7–9].

The commercial drug acetaminophen is nowadays produced in large scale via Hoechst-Celanese process based on the Beckmann rearrangement of 4-hydroxyacetophenone oxime catalyzed by thionyl chloride [5].

Other synthetic approach employs ionic liquids in combination with Lewis acids in two stages but work-up steps are required, similarly [13,14].

The use of organic compounds to promote the Beckmann rearrangement has long been known, [15,16], however trifluoroacetic acid (TFA) has been employed in the Beckmann rearrangement only for activated oxime carbonate [17].

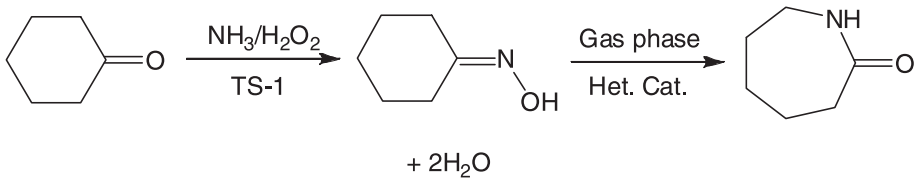
Recently, we have reported the use of TFA as organo-catalyst for the Beckmann rearrangement of keto-oxime to amides [18–21]. The proposed reaction mechanism envisages the formation of the oxime ester of the TFA, which, after rearrangement, forms a trifluoroacetyl amide. The latter is the catalytic active species, see Scheme 2 [18–21].

An efficient one-pot synthesis of caprolactam from cyclohexanone in TFA/CH_3CN in the presence of a moderate excess of hydroxylamine hydrochloride (HOA) has been reported by Luo and coworkers [22,23]. Recently, we have reported an improved synthetic procedure that employed solventless reaction condition and we successfully tested its general application on several ketones and aldehyde [24].

Direct oxiamation-Beckmann rearrangement of cyclohexanone to ε-caprolactam has also been achieved in liquid phase reaction starting from cyclohexanone, ammonia and air in the presence of bifunctional

* Corresponding author at: Department of Molecular Science and Nanosystems, Ca' Foscari University, 2137 Dorsoduro, 30123 Venice, Italy. Tel.: +39 041 2348626; fax: +39 041 2348517.
E-mail address: ronchin@unive.it (L. Ronchin).

http://dx.doi.org/10.1016/j.catcom.2014.05.007
1566-7367/



Scheme 1. Enichem–Sumitomo process for the production of -caprolactam.

catalysts [25,26]. This complex three-step reaction (ammonia oxidation to hydroxylamine, oximation of cyclohexanone and Beckmann rearrangement of the cyclohexanone oxime) gives caprolactam in moderate yield (40–50%) and the procedure has not been investigated on different ketones.

One-pot synthesis of amides from ketones by microwave irradiation was also observed with selected ketones by Feng and coworkers in moderate yield [27]. Several metal-catalyzed one-pot syntheses of amides from aldehyde have been also reported although these processes require either long reaction time, high temperature or toxic solvents [28,29]. Sharghi and Sarvari reported that TiO_2 catalyzes the one step oximation Beckmann rearrangement in solventless condition in good yield [30].

In this work we account for the first time on the self-catalyzed amination of ketones to amides by using hydroxylamine hydrochloride as the amination agent in the absence of any additional acids or bases. Employing this new reaction condition 4-hydroxyacetanilide (AcP), (acetaminophen drug), was synthesized via 4-hydroxyacetophenone (4-HAP). Furthermore, the procedure was applied for the preparation of industrially relevant intermediates acetanilide (AcA) via acetophenone (AP) and caprolactam (CPL) via cyclohexanone (CyC) [5].

2. Experimental

For materials and more experimental details see supplementary materials.

All the reactions were carried out in a well stirred pressurized glass reactor thermostatted at temperatures comprised between 70 °C and 110 °C containing weighed samples of the solvent and reagents typically 1.5 mmol of the selected ketone, 4.4 mmol of HOA and in some cases 22 mmol CH_3CN.

Reaction products were analyzed by Gas Cromatograph (GC), Gas Cromatograph coupled mass spectroscopy (GC–MS) and by high performance liquid chromatography (HPLC). The ^1H nuclear magnetic resonance (NMR) spectra were recorded at 298 K, referred to tetramethylsilane.

3. Results and discussion

Table 1 shows the reactivity of selected aldehydes and ketones with HOA without the use of any additional acid and in acetonitrile as solvent. Aldehydes resulted generally more reactive than ketones, likely because of the easiest attack of HOA, and they are mainly converted into nitriles [31]. On the other hand, ketones gave as main product amides. Thus, in these reaction conditions, benzaldehyde was easily converted into benzonitrile in high yield (entry 1, Table 1); benzamide was detected only in traces, meanwhile the main by-product was benzoic acid [31]. A similar reactivity was observed for 4-nitrobenzaldehyde (entry 2, Table 1), which formed mainly 4-nitrobenzonitrile.

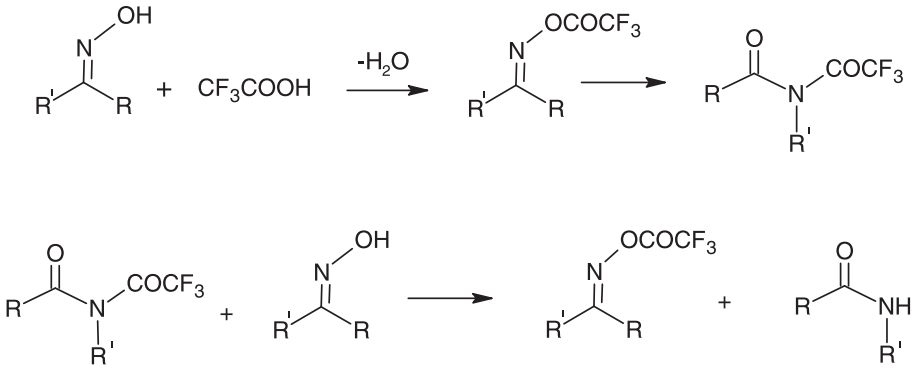
4-Isopropyl benzaldehyde and 2-hydroxy benzaldehyde (entries 3 and 4 Table 1) gave almost quantitative conversion and high selectivity toward the corresponding benzonitrile. The negligible substituent effect is likely due to the high activity of the aldehyde compared to ketones.

When heptanal was employed as starting material the reaction resulted in the complete conversion of the substrate, however, the selectivity toward the amidation products was only moderate (*ca* 50% entry 5, Table 1), this due probably to the even higher reactivity of aliphatic aldehyde compared to the aromatic ones.

As the above mentioned ketones showed only a moderate conversion to oximes, amides were the only rearrangement product. For instance, in the studied reaction conditions, the conversion of AP after 15 h resulted as high as 95%, while without solvent is quite modest (33%, entry 6, Table 1). In addition, the selectivity toward AcA was 85% and acetophenone oxime is present in trace amounts. On the contrary, without solvent the starting ketone was mainly converted into the corresponding oxime (80%). Most probably the beneficial effect of CH_3CN could be ascribed to reagent solubility, especially that of HCl (the acid catalyst of the Beckmann rearrangement) resulting from HOA nucleophilic attack of the ketone.

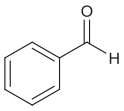
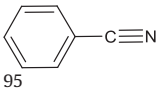
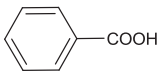
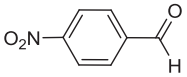
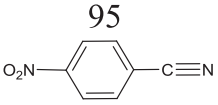
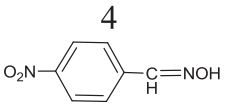
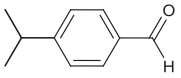
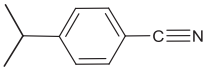
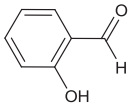
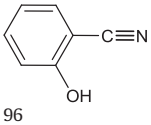
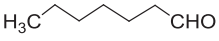
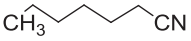
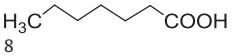
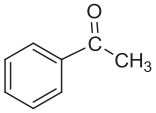
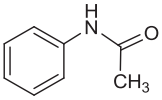
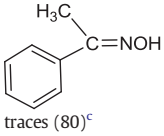
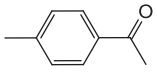
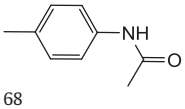
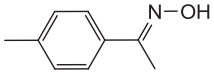
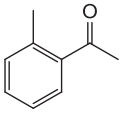
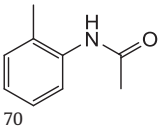
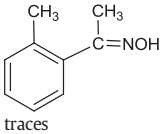
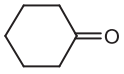
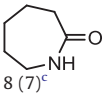
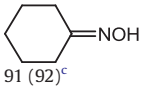
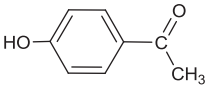
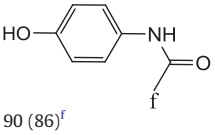
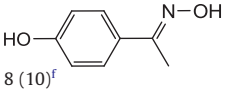
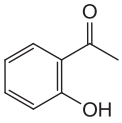
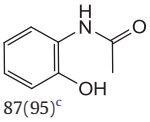
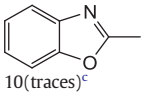
4-Methylacetophenone and 2-methylacetophenone both resulted quite reactive giving the corresponding amide in 70% of selectivity (entries 7 and 8, Table 1). The main difference between the two molecules is that 4-methylacetophenone gave also 20% of the corresponding oxime as by-product, while 2-methylacetophenone was partially converted into the corresponding amine and some oxidation products. This different behavior might be ascribed to the reactivity of the two ketoxime (the intermediate) in the Beckmann rearrangement. In fact 2-methylacetophenone rearranges more easily compared to 4-methylacetophenone [16,32].

The reactivity of CyC in the presence and in the absence of CH_3CN was also investigated (entry 9, Table 1). In this case the presence of the solvent does not influence the reaction outcome. In both



Scheme 2. Reaction mechanism of TFA catalyzed Beckmann rearrangement of ketoximes to amides.

Table 1
Reactivity of selected aldehydes and ketones with HOA. Reaction conditions: substrate 10 mmol, OHA 30 mmol at 70 °C, time of reaction 15 h, CH_3CN 100 mmol.

Entry	Substrate	Conv. %	Selectivity %		Other products %
1		99	 95	 4	1[a]
2		99	 94	 5	1[a]
3		99	 97	/	3[a]
4		98	 96	/	4[a]
5		99	 50	 8	42[a]
6		95[b] (33)[c]	 85(10)[c]	 traces (80)[c]	14[d] (10)[c,d]
7		92	 68	 19	13[d]
8		95	 70	 traces	29[d]
9		82 (80)[c]	 8 (7)[c]	 91 (92)[c]	1[e] (1)[c,e]
10		90 (89)[f]	 90 (86)[f]	 8 (10)[f]	2 (4)[f]
11		14(4)[c]	 87(95)[c]	 10(traces)[c]	3 (5)[c]

[a] Mainly acids, esters and condensation products.
[b] Employng a HOA/AP = 1, conversion 91% amide selectivity 86% more details in supplementary materials.
[c] Reaction carried out in the absence of solvent.
[d] Mainly amines and oxidation and condensation products.
[e] Products of CyC oxidation and condensation.
[f] Employng a HOA/4HAP = 1.

experiments the main product observed was COX. This behavior can be due to a more difficult Beckman rearrangement of COX compared to those of aromatic ketones, this may explain the low selectivity to caprolactam [16,32]. In this way, the beneficial effect of CH_3CN is negligible, since it is likely that HCl acidity is not sufficient to catalyze Beckmann rearrangement, under these experimental conditions.

4-HAP, under the same reaction conditions, showed high conversion of the ketone (90%). The main product formed was AcP (entry 10, Table 1) and the rest was practically 4-hydroxyacetophenone oxime, (4-HAPO). It is noteworthy that the reaction was very selective (by-products less 2%).

2-Hydroxyacetophenone, on the other hand, showed a lower conversion, but the selectivity to the corresponding amide remains almost ate 90% (entry 11, Table 1). The hydroxyl group in 2-position has a negative effect on the attack of the HOA thus diminishing the conversion of the ketone, but the reason of this behavior is not clear and it could be connected with both its steric hindrance, as well as with the presence of intermolecular hydrogen bonds between 2-HAP and HOA. These

Table 2
Reactivity of 4-HAP with HOA. Reaction conditions: 4-HAP 10 mmol, HOA 30 mmol.

Entry	Temp. °C	Time h	Solvent Molar ratio		Conversion %	Selectivity %		
			CH_3CN	H_2O		4-HAPO	AcP	Notes
1	90	15	10	/	99	1.0	88	Pitches
2	90	1	10	/	96	4	96	/
3[a]	90	1	10	/	99	99	/	/
4[a]	90	15	10	/	97	96	3.7	/
5	90	1	/	20	78	40	60	/
6	90	15	/	20	51	64	34	Pitches
7	100	5	10	/	99	/	97	Pitches
8	100	1	10	/	96	Traces	98	/
9	110	15	10	/	99	/	/	Pitches
10	110	1	/	/	98	1	97	/
11	110	15	/	/	99	Traces	Traces	Pitches

[a] Reaction carried out in the presence of 4 equivalents of pyridine with respect to 4-HAP.

Table 3
Reactivity of AP with HOA. Run conditions: AP 10 mmol, HOA 30 mmol.

Entry	Temp. °C	Time h	Reagents Molar ratio		Conversion %	Selectivity %			
			CH_3CN	H_2O		APO	AcA	Anl	Notes
1[a]	90	15	10	/	99	98	/	/	/
2	90	1	10	/	86	9	71	12	Products[b]
3	90	15	10	/	99	/	89	10	Products[b]
4	90	15	/	/	73	83	5	Traces	Pitches[c]
5	90	15	/	20	20	99	/	/	Biphasic
6	100	1	/	20	42	82	/	/	Pitches
7	100	15	/	20	93	80	/	/	Pitches
8	100	1	10	/	99	/	83	17	/
9	100	3	10	/	99	/	81	18	Pitches
10	100	5	10	/	99	/	78	19	Pitches
11	110	1	10	/	99	/	79	19	Pitches
12	110	15	10	/	99	/	8	24	Pitches
13	110	1	/	/	20	95	Traces	Traces	Pitches
14	110	15	/	/	95	5	Traces	54	Pitches

[a] Reaction carried out in the presence of 4 equivalents of pyridine with respect to AP.
[b] Products are condensation and chlorinated compounds.
[c] Pitches are insoluble brown to black condensation products of complex structure.

are however conjectures whose explanation is beyond the scope of the present work. The formation of the benzoxazole with 2-hydroxyacetophenone is a consecutive reaction, which occurs after the rearrangement (Table 1 entry 11). This result suggests that the hydroxyl group position does not strongly affect the Beckmann rearrangement although it influences the reaction selectivity promoting the subsequent benzoxazole formation.

Table 2 accounts on the reactivity of 4-HAP in the presence of OHA under various reaction conditions. As already shown in Table 1 (entry 10), at 70 °C the substrate resulted almost completely converted (90%) with 90% selectivity toward the AcP, some unconverted ketone and 4-HAPO are also present in the reaction mixture.

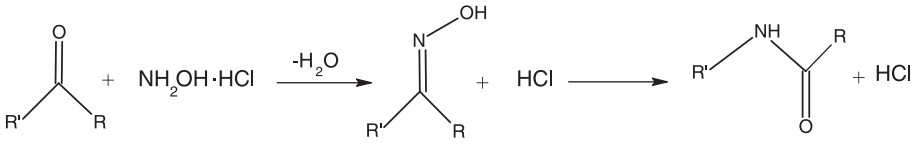
Both temperature and reaction time are relevant parameters for the reaction outcome especially for very reactive substances such as OHA, 4-HAP and AcP, that might undergo several consecutive and parallel reactions. It is noteworthy that when increasing temperature to 100 °C the selectivity toward AcP increases (entry 8, Table 2) although it is necessary to control reaction time in order to avoid formation of pitches and condensation products (entry 7, Table 2). In fact, long time of reaction causes extensive formation of pitches because both reagent and product are thermally sensible [20]. In this reaction the presence of CH_3CN seems necessary to solubilize reagents and products, although when the amidation was performed in solventless at 110 °C (melting point 4-HAP 108 °C), both conversion and selectivity toward AcP were almost quantitative (98% and 97% respectively), after 1 h of reaction (entry 10, Table 2).

From a mechanistic point of view it is likely that the reaction proceeds via oxime formation followed by its Beckmann rearrangement to the desired amide (Scheme 3). As a matter of fact, 4-HAPO is always observed in the reaction mixture as being a stable reaction intermediate whose rearrangement gives AcP. In addition, the reactivity of *ortho*-hindered acetophenones, such as 2,4-dimethylacetophenone or 2,4,6-trimethylacetophenoe, does not give either oximes or amides (see supplementary information). This is a further evidence that amide is formed via the oximation step, which is, not allowed to *ortho*-hindered acetophenones under such conditions.

In this reaction conditions $NH_2OH{\cdot}HCl$ acts as amination agent and an in situ catalyst. In fact, subsequent to the formation of the oxime a molecule of HCl is released and can thus catalyze the Beckmann rearrangement according to Scheme 3. The role of HCl as an in situ catalyst for the Beckmann rearrangement step is confirmed by the reactions carried out in the presence of pyridine, employed as HCl scavenger (entries 3 and 4, Table 2), that gave selectively 4-HAPO without any AcP formation.

When water was used as solvent it caused a neat decreasing in the 4-HAP conversion (entries 5 and 6, Table 2). In fact, at 90 °C after 1 h of reaction only 34% of conversion and 10% of selectivity toward AcP were observed. Furthermore, after 15 h of reaction, it was achieved a moderate conversion (51%) and a poor selectivity to AcP (34%). However in these reaction conditions, i.e., in the presence of water, a rather high selectivity to 4-HAPO (80% after 1 h of reactions and 64% after 15 h of reactions) was observed. This suggests that the inhibiting effect of water is more significant on the Beckmann rearrangement stage than on the oximation step. In fact, the Beckmann rearrangement occurs when nitrogen is positively polarized and this is induced by HCl protonation, whose ability decreases by dilution in water [33,34]. This is confirmed by the comparison of the reactivity of AP, 4-HAP and CyC, in water as solvent (Tables 2 entries 5, 6, Table 3 entries 5, 7, Table 4 entries 6 and 7), these results confirm that only 4-HAP gives a certain selectivity to amide being the intermediate oxime that requires less acidity to rearrange. When the reaction was carried out at 100 °C almost quantitative conversion and selectivity of 97–99% were observed (entries 7 and 8, Table 2), however longer reaction time may cause decomposition of the product which is a thermal sensible compound. It is noteworthy, that the reaction occurs in solventless conditions with 98% conversion and 97% selectivity to AcP, after 1 h of reaction (entry 10, Table 2). Also in this case, the control of the reaction time is critical as the high temperature needed to melt 4-HAP (108 °C *ca.*) may cause extensive decomposition at long reaction time (entry 11, Table 2).

Table 3 shows the reactivity of AP with $NH_2OH{\cdot}HCl$ under various reaction conditions. The reaction proceeds similarly to the one of 4-HAP, even though the selectivity toward the amide is generally lower. Also in this case the presence of pyridine inhibits the rearrangements and only APO was observed. AP can be achieved in almost quantitative conversion in the presence of CH_3CN as solvent (15 h) with a selectivity



Scheme 3. Reaction path of ketone amidation.

Table 4
Reactivity of CyC with HOA. Run conditions: CyC 10 mmol, HOA 30 mmol.

Entry	Temp. °C	Time h	Reagents Molar ratio		Conversion %	Selectivity %		
			CH_3CN	H_2O		COX	CPL	Notes
1[a]	90	15	10	/	99	98	/	Pitches[b]
2	90	1	10	/	79	44	14	Byproducts[c]
3	90	15	10	/	95	56	25	Pitches, byproducts
4	90	1	/	/	71	41	15	Byproducts
5	90	15	/	/	93	66	11	Pitches, byproducts
6	90	1	/	20	60	61	/	Byproducts
7	90	15	/	20	77	79	5	Biphasic, byproducts
8	100	1	10	/	76	54	39	Pitches, byproducts
9	100	3	10	/	90	23	72	Pitches, byproducts
10	100	5	10	/	94	5	61	Pitches
11	110	1	10	/	92	13	61	Pitches, byproducts
12	110	15	10	/	99	/	/	Pitches
13	110	1	/	20	62	85	5	Byproducts
14	110	1	/	/	90	85	1	Byproducts
15	110	15	/	/	98	/	/	Pitches

[a] Reaction was carried out in the presence of 4 equivalents of pyridine with respect to COX.
[b] Pitches are insoluble brown to black condensation products of complex structure.
[c] GC–MS analysis showed several products of condensation, isomerization and various chlorinated compounds.

to AcA ranging from 80 to 90% (entries 3, 8–11, Table 2). The main byproduct of the reaction is aniline (Anl), thus suggesting that reaction proceeds in almost quantitative conversion to AcA, but deacetylation (likely via hydrolysis) of AcA to Anl occurs as a consecutive reaction after the rearrangement. The decrease in AcA selectivity is also accompanied by the continuous increase of the pitches over time, whose composition, studied by GC–MS analysis, shows variable mixtures of phenylaniline, quinone immine and a complex mixture of condensation and chlorination products. The nature of these pitches is similar to that of aniline-black dyes obtained from Anl oxidation, [35].

The reactions carried out in the presence of water as a solvent (entries 5–7, Table 3), showed low conversion and APO as the only major product. This suggests that the presence of water is even more critical for the Beckmann rearrangement of APO (for comparison with 4-HAPO see entries 5 and 6, Table 2). As a matter of fact, it is likely that the acidity of the HCl, released after the oximation, in water is not sufficient to achieve APO rearrangement.

When the reaction was attempted in solventless conditions it appears that at 90 °C, after 15 h a moderate conversion and a very low selectivity in AcA (*ca.* 5%) was obtained (entry 4, Table 3). At 110 °C the rearrangement appeared to be negligible, in fact, after 1 h of reaction APO selectivity is 95%, AcA is detected only in traces, and the rest is mainly condensation products (entry 13, Table 3). At the same reaction condition but longer reaction time (15 h) the conversion was 95%, but the selectivity to APO is decreased to 5%, AcA is present as traces, Anl is the main product reaching 54% of selectivity, and pitches and heavy condensation products are also present in the reaction mixture (entry 14, Table 3). The presence of Anl suggests that the Beckmann rearrangement occurs, but the negligible selectivity to AcP is due to consecutive and parallel reactions, which are responsible of AcP consumption.

In Table 4 the reactivity of CyC with HOA is reported. Also in this case the presence of HCl appears essential to achieve CPL since COX was the only product formed in the presence of pyridine (entry 1, Table 4). Under the same reaction conditions, the conversion of CyC was lower than that of the aromatic ketones (4-HAP and AP). As a matter of fact, in the case of CyC the Beckmann rearrangement step appears to be more inhibited compared to the aromatic ketones. This is in agreement with the relative reactivity of the corresponding oximes to the Beckmann rearrangement in mineral acid [16,32].

The selectivity to CPL are generally not comparable with those of the aromatic ketones because cyclohexanone has strong tendencies to condense, therefore the control of the reaction parameters is even more crucial to achieve high selectivity to the desired product. Even though, the optimization of the reaction condition is beyond the scope of this preliminary work it is evident that under the proper condition CyC may show both high conversion and synthetically interesting selectivity to CPL (entry 11, Table 4). Compared to data reported in Table 1, where CH_3CN did not seem to influence the selectivity, here, the solvent could play an important role in the reaction outcome (entries 1, 3, 4, 9–13, Table 4). In fact, only in the presence of CH_3CN the selectivity to CPL reaches values interesting from a synthetic point of view. For instance, at 90 °C, after 3 h of reaction and in the presence of CH_3CN as a solvent/promoter, it was achieved a conversion of 90% with 72% selectivity toward CPL. In the absence of solvent, the reaction resulted in only a modest selectivity toward amides (entries 4, 5, 14 and 15, Table 4). Most probably, the large amount of pitches observed also at low temperature might inhibit the acid catalyzed Beckmann rearrangement. As a matter of fact, oximation of ketone to COX occurred, but the HCl formed, necessary for its rearrangement, is consumed in other side reactions. This is in agreement with the presence of chlorinated compounds detected by GC–MS analysis. The negligible selectivity to CPL and the quite high selectivity to COX observed in the presence of water (entries 7 and 8, Table 4) suggest that the rearrangement needs an acidity higher than that achieved by the HCl, formed during the oximation step, in the presence of water [33,34].

4. Conclusion

In this work we report for the self-catalyzed direct amidation of ketones. The conversion of various ketones to amides has been investigated. Results achieved are particularly interesting for the substrates, whose production presents environmental and plant concerns that could be solved by an industrial implementation of this reaction. It is noteworthy that in these reaction conditions, acetaminophen could be obtained in one-pot from 4-hydroxyacetophenone oxime in almost quantitative yield without any solvent or acid catalyst.

Acetanilide and caprolactam were also obtained in high yields in the presence of CH_3CN which is an easily recyclable solvent.

The reaction appears to follow the one-pot oximation-Beckmann rearrangement reaction path; a two stage process whose steps are well known reactions. In this way, the control of the overall process for industrial application appears to be easy and of simple implementation.

Acknowledgments

Financial support by Ca' Foscari University of Venice is gratefully acknowledged (ADIR fund 2011). A special thanks to Mr. Claudio Tortato for the helpful discussions.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2014.05.007.

References

[1] R. Opsahl, Amides "Fatty acid", 4th ed., Kirk Othmer Encyclopedia of Chemical Technology, vol. 2, J. Wiley, 1999.
[2] M.M. Goldenberg, R.M. Joyce, Analgesic and antipyretics, Ulmann Encyclopaedia of Industrial Chemistry, 6th ed., J. Wiley, 1998.
[3] R.M. Lanigan, T.D. Sheppard, Eur. J. Org. Chem. (2013) 7453–7465.
[4] R.A. Nugent, C.H. Hall, Analgesics, antipyretics and antinflammatory agents, 4th ed., Kirk Othmer Encyclopedia of Chemical Technology, vol. 2, J. Wiley, 1999.
[5] K.G. Davenport, C.B. Hilton to Celanese Co. U.S. Pat. 4,524,217 A 1985; Horlenko, T.; Fritch., J. R.; Fruchey, O. S. to Hoechst Celanese Corporation, U.S. Pat. 4,954,652 1990.
[6] W.B. Fisher, L. Crescentini, Caprolactam, 4th ed., Kirk Othmer Encyclopedya of Chemical Technology, vol. 4, J. Wiley, 1999.
[7] G. Petrini, G. Leonfanti, M.A. Mantegazza, F. Pignataro, in: P.T. Anastas, T.C. Williamson (Eds.), Green Chemistry, American Chemical Society, 1996, pp. 33–48.
[8] S. Tonti, P. Roffia, V. Gervasutti, to Enichem Anic S.p.A., Eu. Pat. 0496385A1, (1992). a) H. Ichihashi, M. Kitamura, H. Kajlkurl, E. Tasaka, US patent. 5,354,859. (1994) to Sumitomo Chemical Co. Ltd.; b) M. Kitamura, H. Ichihashi, H. Tojima, US patent. 5,403,801 (1995) to Sumitomo Chemical Co. Ltd.; d) M. Kitamura, Y. Shimazu, M. Yako, US patent. 6,265,574 (2001) to Sumitomo Chemical Co. Ltd.; e) W.F. Holderich, G. Dahloff, H. Ichihashi, K. Sugita, to Sumitomo Chemical Company US Pat. 6,531,595 B2, 2003.
[9] G. Dahlhoff, J.P.M. Niederer, W.F. Hölderich, Catal. Rev. Sci. Eng. 43 (2001) 381-441. T. Okubo, S. Suzuki, T. Matsushita, T. Suzuki, to Sumitomo Chemical Co, Eu. Pat. 2,157,080, (2009). W.F. Hoelderich, A. Mettu, R. Schaller, to Uhde/Inventa/Fischer EP 2098506 (2008).
[10] Y. Ogata, M. Okano, K. Matsumoto, J. Am. Chem. Soc. 77 (1955) 4643–4646.
[11] F. Greer, D.E. Pearson, J. Am. Chem. Soc. 77 (1955) 6649–6650.
[12] M.I. Vinnik, N.G. Zarakhani, Russ. Chem. Rev. 36 (1967) 51–64.
[13] X. Liu, L. Xiao, H. Wua, Z. Li, J. Chen, C. Xia, Catal. Commun. 10 (2009) 424–427.
[14] A. Zicmanis, S. Katkevica, P. Mekss, Catal. Commun. 10 (2009) 614–619.
[15] L. De Luca, G. Giacomelli, A. Porcheddu, J. Org. Chem. 67 (2002) 6272.
[16] J.K. Augustine, R. Kumar, A.B. Ashis, B. Mandal, Tetrahedron Lett. 52 (2011) 1074–1077.
[17] S. His, C. Meyer, J. Cossy, G. Emeric, A. Greine, Tetrahedron Lett. 44 (2003) 8581–8584.
[18] L. Ronchin, A. Vavasori, M. Bortoluzzi, Catal. Commun. 10 (2008) 251–256.
[19] L. Ronchin, M. Bortoluzzi, A. Vavasori, J. Mol. Struct. Theochem 858 (2008) 46–51.
[20] L. Ronchin, A. Vavasori, J. Mol. Catal. A Chem. 313 (2009) 22–30.
[21] E. Rancan, G. Quartarone, L. Ronchin, A. Vavasori, Appl. Catal. A Gen. 472 (2014) 167–177.
[22] J. Zhang, Y. Lu, K. Wang, G. Luo, Ind. Eng. Chem. Res. 52 (2013) 6377–6381.
[23] J.S. Zhang, A. Riaud, K. Wang, Y.C. Lu, G.S. Luo, Catal. Lett. 144 (2014) 151–157.
[24] F. Aricò, G. Quartarone, E. Rancan, L. Ronchin, P. Tundo, A. Vavasori, Catal. Commun. 49 (2014) 47–51.
[25] R. Mokaya, M. Poliakoff, Nature 437 (2005) 1243–1244.
[26] J.M. Thomas, R. Raja, Proc. Natl. Acad. Sci. 102 (2005) 13732–13736.
[27] J.C. Feng, B. Liu, L. Dai, Chin. Chem. Lett. 9 (1998) 795–796.
[28] A. Martínez-Asencio, M. Yus, D. Ramón, Tetrahedron 68 (2012) 3948–3951.
[29] M. Ashif, T. Punniyamurthy, Adv. Synth. Catal. 352 (2010) 288–292.
[30] H. Sharghi, M. Hosseini-Sarvari, J. Chem. Res. Synop. (2003) 176–178.
[31] E.C. Horning, V.L. Stromberg, H.A. Lloyd, J. Am. Chem. Soc. 74 (1952) 5153–5155.
[32] N.C. Marziano, L. Ronchin, C. Tortato, O. Tonon, R. Bertani, Int. J. Chem. Kinet. 36 (2004) 417–426.
[33] C.H. Rochester, Acidity Functions, Academic Press, London, 1970.
[34] N.C. Marziano, L. Ronchin, C. Tortato, A. Zingales, A.A. Sheikh-Osman, J. Mol. Catal. A Chem. 174 (2001) 265–277.
[35] T. Klausen, in: K. Hunger (Ed.), Industrial Dyes, Wiley VCH, 2003, pp. 473–484.