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JSCS–4636 *Short communication*

SHORT COMMUNICATION

K-10 clay as a reusable catalyst for the solvent-free, MW-induced synthesis of enaminones

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Abstract: A series of *β*-amino-*α*,*β*-unsaturated ketones and esters were synthesized in good to excellent yields from the reaction of different amines with 1,3-dicarbonyl compounds in solvent-free media using montmorillonite K-10 clay as a solid recyclable heterogeneous acidic catalyst and microwave irradiation.

Keywords: montmorillonite K-10 clay; *β*-amino-*α*,*β*-unsaturated esters and ketones; solvent-free; microwave.

INTRODUCTION

β-Amino-*α*,*β*-unsaturated esters and ketones are useful synthetic intermediates,[1] particularly in the construction of heterocyclic compounds such as dihydropyridines,[2–5] pyridines,[6] pyrimidines,[7] indoles,[8] isothiazoles,[9] oxazolidinones, pyrrole and *α*-amino-*β*-lactams.[10–13] A number of reviews have been published concerning the chemistry of *β*-amino-*α*,*β*-unsaturated esters and ketones, their hydrolysis, physicochemical properties and uses.[14] The standard methods for the preparation of *β*-enamino ketones involve the direct condensation of amines and diketones using a stream of gaseous amine, ammonium acetate and reflux in aromatic solvent with azeotropic removal of the water[15] or the reaction of a lithiated Schiff's base from imines with esters.[16] Consequently, the development of more efficient methods and exploring proper reagents as catalysts are still in demand to make the available procedures more convenient and simple.

Application of naturally benign substances like montmorillonite clays as catalysts for chemical reactions constitutes an exciting component of green

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chemistry. The use of K-10 clay as solid support has become very useful in synthetic organic chemistry because of its enhanced selectivity due to its lamellar swelling structure, large surface area, the availability of both Brønsted and Lewis surface acidic sites, milder reaction conditions and ease of workup.[17] The combined use of montmorillonite and microwave irradiation (MWI) showed rate enhancements, high yields and short reaction times. In addition, the use of solvent-free conditions with heterogeneous media under microwave irradiation is a useful alternative and has received considerable attention due to its greater efficiency from economic as well as ecological points of view.[18]

In continuation of ongoing investigations exploring the use of montmorillonite as a solid support in the synthesis and reactivity of organic compounds using microwave irradiation,[19] this paper reports a simple, selective and environmentally acceptable microwave promoted synthesis of *β*-amino-*α*,*β*-unsaturated esters and ketones using montmorillonite K-10 clay as an efficient heterogeneous acid catalyst.

RESULTS AND DISCUSSION

As shown in Table I, a variety of *β*-amino-*α*,*β*-unsaturated esters and ketones were obtained using this procedure and no by-products were observed. In general, for a wide variety of amines, the condensation reactions usually afforded the corresponding *β*-amino-*α*,*β*-unsaturated esters and ketones in over 90 % yields in a short reaction time (Scheme 1). The presence of an electron-withdrawing group on the benzene ring decreased the reactivity of the substrate (entry 14). The solid clay portion applied in the first cycle was washed with methanol and dried at 120 °C under reduced pressure to be reused in the subsequent reactions, which showed a gradual decrease in the activity (Table I).

TABLE I. K-10 clay supported microwave-induced synthesis of *β*-amino-*α*,*β*-unsaturated esters and ketones

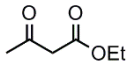
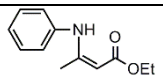
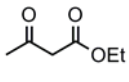
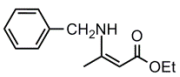
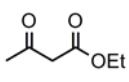
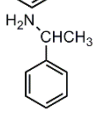
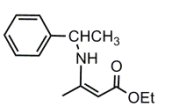
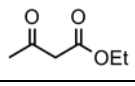
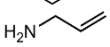
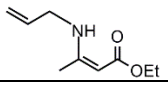
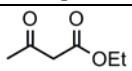
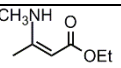
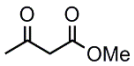
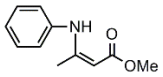
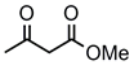
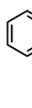
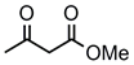
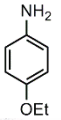
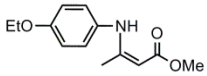
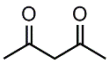
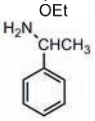
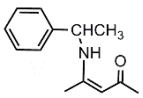
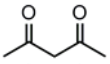
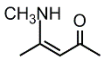
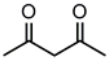
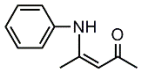
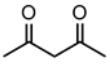
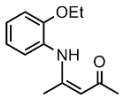
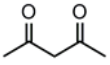
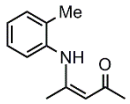
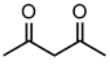
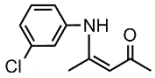
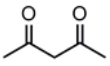
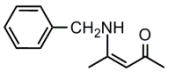
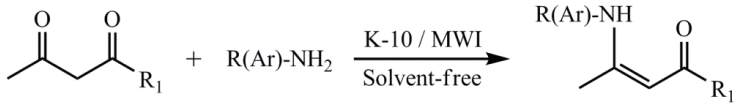
Entry	Dicarbonyl Compound	Amine	Product[a]	Yield, %[b]	Time, min
1				96 (92)	2
2				98 (91)	2.5
3				95 (89)	3
4				96 (92)	2.5

TABLE I. Continued

Entry	Dicarbonyl Compound	Amine	Product[a]	Yield, %[b]	Time, min
5				96 (90)	2.5
6				98 (95)	2
7				95 (91)	2.5
8				94 (90)	2.5
9				92 (87)	2.5
10				94 (90)	2.5
11				95 (92)	2
12				97 (92)	3
13				95 (88)	3
14				87 (82)	3.5
15				92 (88)	2.5

[a]All products were identified by comparison of their physical and spectral data with those of authentic samples;[20] [b]isolated yields. Yields indicated in the parenthesis correspond to those reactions in which recovered K-10 clay was used. The fresh solid clay portion applied in the first cycle, was filtered off, washed with methanol (2×30 mL) and dried at 120 °C under reduced pressure to be reused in the subsequent reaction



R_1: OEt, OMe, Me

Scheme 1. Synthesis of *β*-amino-*α*,*β*-unsaturated esters and ketones on K-10 clay under MWI.

EXPERIMENTAL

General

Melting points were determined on an Electrothermal 9100 apparatus. The ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a FT-NMR BRUKER DRX 500 Avance spectrometer. Chemical shifts were measured in ppm from TMS. $CDCl_3$ was used as the solvent as well as the internal standard. The IR spectra were recorded on a Perkin-Elmer FT-IR GX instrument in KBr discs. Physical and spectral data of the synthesized compounds are given in the Supplementary material to this paper.

Microwave irradiations were realized with a Synthewave 402® (Prolabo, France) single mode focused microwave reactor.[21] The chemicals used in this work were purchased from Merck and Fluka.

Typical procedure

In a typical experiment (entry **11**), acetylacetone (3 mmol) and aniline (5 mmol) were dispersed on K-10 clay (1 g). The heterogeneous mixture was submitted into a single mode focused microwave reactor with continuous rotation for 3 min (optimized time) at 40 °C. The product was extracted by washing the K-10 clay with ethyl acetate. The organic layer was washed with water, dried with $MgSO_4$, filtered and the solvent was removed under vacuum to afford the relevant *β*-amino-*α*,*β*-unsaturated ketone **11**.

CONCLUSIONS

In conclusion, the supported reaction using K-10 clay and MWI provides a general procedure for a highly selective method for the synthesis of *β*-amino-*α*,*β*-unsaturated esters and ketones. The major advantages of this methodology are mild reaction conditions and faster reaction rates. The K-10 clay catalyst is inexpensive, non-toxic and reusable, which makes the process convenient, more economic and benign. The notable features of this procedure are the solvent-free conditions, high yields of products, cleaner reaction profiles, and availability of the reagents.

SUPPLEMENTARY MATERIAL

Physical and spectral data of the synthesized compounds are available electronically at http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

Acknowledgment. Financial support from Payam Noor University (PNU), Roodsar, Guilan, Iran is gratefully appreciated.

ИЗВОД

ГЛИНА К-10 КАО КАТАЛИЗАТОР СА ВИШЕКРАТНОМ УПОТРЕБОМ ЗА СИНТЕЗУ ЕНАМИНОНА ПОД УСЛОВИМА ГРЕЈАЊА МИКРОТАЛАСИМА У ОДСУСТВУ РАСТВАРАЧА

OMID MARVI[1], MASOUD GIAHI[2], POURAN PUR AYUB[1] и MOHAMMAD NIKPASAND[3]

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Извршена је синтеза серије *β*-амино-*α*,*β*-незасићених кетона и естара реакцијом различитих амина и 1,3-дикарбонилних једињења, у одсуству растварача, коришћењем

монморијонит K-10 глине, као чврстог катализатора са вишекратном употребом, под условима загревања реакционе смеше микроталасима. Производи су добијени у добром до одличном приносу.

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REFERENCES

1. J. V. Greenhill, *Chem. Soc. Rev.* **6** (1977) 277
2. H. H. Fox, J. I. Lewis, W. J. Wenner, *Chem. Soc*. (1951) 1259
3. J. E. Arrowsmith, S. F. Campbell, P. E. Cross, J. K. Stubbs, R. A. Burges, *J. Med. Chem.* **29** (1986) 1696
4. D. Alker, S. F. Campbell, P. E. Cross, R. A. Burges, A. J. Carter, *J. Med. Chem.* **33** (1990) 1805
5. K. Miyashita, M. Nishimoto, T. Ishino, H. Murafuji, S. Obika, O. Muraoka, T. Imanishi, *Tetrahedron* **53** (1997) 4279
6. G. Horlein, B. Kubel, A. Studeneer, G. Salbeck, *Liebigs Ann. Chem.* (1979) 371
7. K. Grohe, H. Heitzer, *Liebigs Ann. Chem.* (1973) 1025
8. D. Raileaunu, M. Palaghita, C. D. Nenitzescu, *Tetrahedron* **27** (1971) 5031
9. R. K. Howe, T. A. Grumer, L. G. Garter, J. E. Frans, *J. Heterocycl. Chem.* **15** (1978) 1001
10. C. M. Kascheres, *J. Braz. Chem. Soc.* **14** (2003) 945
11. G. Negri, C. Kascheres, A. J. Kascheres, *J. Heterocycl. Chem.* **41** (2004) 461
12. H. M. C. Ferraz, F. L. C. Pereira, *Quim. Nova* **27 (**2004) 89
13. H. K. Hombrecher, G. Horter, *Synthesis* (1990) 389
14. a) A.-Z. A. Elassar, A. A. El-Khair, *Tetrahedron* **59** (2003) 8463; b) J. P. Michael, C. B. De Koning, D. Gravestock, G. D. Hosken, A. S. Howard, C. M. Jungmann, R. W. M. Krause, A. S. Parsons, S. C. Pelly, T. V. Stanbury, *Pure Appl. Chem.* **71** (1999) 979; c) T. Ueda, H. Konishi, K. Manabe, *Tetrahedron Lett.* **53** (2012) 5171; d) J. Sun, L.-L. Zhang, C.-G. Yan, *Tetrahedron* **69** (2013) 5451; e) M. Youness El Kadiri, E. Framery, B. Andrioletti, *Tetrahedron Lett.* **53** (2012) 6335; f) T. Muraoka, E. Hiraiwa, M. Abe, K. Ueno, *Tetrahedron Lett.* **54** (2013) 4309
15. P. G. Baraldi, D. Simoni, S. Manfredini, *Synthesis* (1983) 902
16. a) G. Bartoli, C. Cimarelli, G. Palmieri, M. Bosco, R. Dalpozzo, *Synthesis* (1990) 895; b) C. J. Valduga, A. Squizani, H. S. Braibante, M. E. F. Braibante, *Synthesis* (1998) 1019
17. a) P. Lasszlo, *Science*, **235** (1987) 1473; b) B. Baghernejad, *Lett. Org. Chem.* **7** (2010) 255; c) S. Agarwal, J. N. Ganguli, *J. Mol. Catal. A: Chem.* **372** (2013) 44; d) N. Kaur, D. Kishore, *J. Chem. Pharm. Res.* **4** (2012) 991; e) M. R. Dintzner, *Synlett* **24** (2013) 1091; f) G. Baishya, B. Sarmah, N. Hazarika, *Synlett* **24** (2013) 1137; g) M. V. Reddy, G. C. S. Reddy, Y. T. Jeong, *Tetrahedron* **68** (2012) 6820; h) K. C. Majumdar, S. Ponra, T. Ghosh, *Synthesis* **44** (2012) 2079; i) W. Chen, M.-X. Zhang, C. Li, Y.-L. Li, *J. Serb. Chem. Soc.* **78** (2013) 537
18. a) P. Lidström, J. Tierney, B. Wathey, J. Westman, *Tetrahedron* **57** (2001) 9225; b) M. E. F. Braibante, H. T. S. Braibante, A. F. Morel, C. C. Costa, M. G. Lima, *J. Braz. Chem. Soc.* **17** (2006) 184; c) *Microwave-Assisted Organic Synthesis*, P. Lidstrom, J. P. Tierney, Eds., Blackwell, Oxford, 2005; d) *Microwave Methods in Organic Synthesis*, M. Larhed, K. Olofsson, Eds., Springer, Berlin, 2006; e) D. Dallinger, C. O. Kappe, *Chem. Rev.* **107** (2007) 2563; f) P. Belov, V. L. Campanella, A. W. Smith, R. Priefer, *Tetrahedron Lett.* **52 (**2011) 2776

19. a) D. Habibi, O. Marvi, *Can. J. Chem.* **85** (2007) 81; b) D. Habibi, O. Marvi, *Catal. Commun.* **8** (2007) 127; c) D. Habibi, O. Marvi, *Arkivoc* (2006) 8; d) D. Habibi, O. Marvi, *J. Serb. Chem. Soc.* **70** (2005) 579; e) D. Habibi, O. Marvi, *Chin. J. Chem.* **26** (2008) 522; f) O. Marvi, M. Nikpasand, *Lett. Org. Chem.* **10** (2013) 353
20. a) Y. Gao, Q. Zhang, J. Xu, *Synth. Commun.* **34** (2004) 909; b) M. E. F. Braibante, H. S. Braibante, L. Missio, A. Andricopulo, *Synthesis* (1994) 898; c) Z.-H. Zhang, Z.-C. Ma, L.-P. Mo, *Indian J. Chem., B* **46** (2007) 535
21. a) Prolabo, Fr. Pat. 62241/D, 14669 FR, December 23th 1991; b) R. Commarmot, R. Didenot, Gardais, JF Rhône-Poulenc/Prolabo Patent No. 84/03496 – October 27th 1986.