HETEROCYCLES, Vol. 68, No. 11, 2006, pp. 2259 - 2267. © The Japan Institute of Heterocyclic Chemistry
Received, 14th July, 2006, Accepted, 2nd October, 2006, Published online, 3rd October, 2006. COM-06-10841

EFFICIENT MICROWAVE ASSISTED SYNTHESES OF UNSUBSTITUTED CYCLIC IMIDES

Yousef M. Hijji * and Ellis Benjamin

Department of Chemistry, Morgan State University, Baltimore, MD 21251.USA.
yhijji@morgan.edu

Abstract – A number of cyclic imides were synthesized from cyclic anhydrides using ammonium chloride (NH_4Cl), and 4-*N*,*N*-dimethylaminopyridine (DMAP) or with ammonium acetate (NH_4OAc) under microwave irradiation in both a mono-mode and a conventional microwave. Several substituted succinic anhydrides used as reactants were synthesized efficiently by Diels-Alder reactions of maleic anhydride with 1,3-cyclohexadienes in 63-82% for the mono-mode and 72-92% in the conventional microwave ovens. Cyclic imides were synthesized with yields from 50 – 98%.

INTRODUCTION

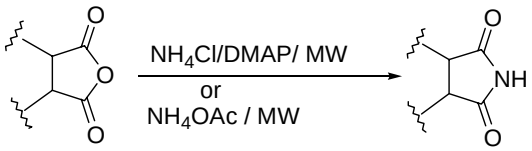
Cyclic imides and their derivatives are important moieties in medicinal, polymeric, photonic, and electronic materials.[1] Often, these imide materials are oxidatively stable, heat retardant, solvent resistant, and physically strong.[2] The conventional syntheses of substituted cyclic imides are well documented in the literature,[3] however the syntheses of *N*-unsubstituted cyclic imides are often limited due to the harsh conditions necessary.[4] There are several conventional synthetic techniques of unsubstituted imides commonly used in the literature. These conditions include the condensation of liquid and/or gas ammonia with cyclic anhydrides,[5] the cyclization of an amide-acid with 1,1'-carbonyldiimidazole (CDI) and DMAP,[6] the reaction of diacid chlorides with lithium nitride,[7] the reaction of a primary and a secondary amide with $AlCl_3$,[8] and the reaction of anhydrides with urea,[9] and formamide.[10] These conditions can often cause low yields, by-product formation and need long reaction times.

The use of microwave technology in many organic reactions has been found to increase the reaction yields, decrease reaction times, and promote reactions under solventless conditions.[11]Of note are the microwave syntheses of *N*-alkyl,[12] amino acid derived[13] cyclic imides, and variety of heterocyclic compounds.[14] The ability to incorporate a novel microwave synthesis for the high yield production of

N-unsubstituted cyclic imides of desired materials is of importance, specifically the ability to incorporate ^{15}N labels into organic molecules in a simple way. Few microwave assisted synthesis were reported to utilize microwave radiation to generate unsubstituted cyclic imides. These syntheses used the reaction of cyclic anhydrides with urea or thiourea,[15] formamide,[16] benzonitrile,[17] and most recently cyanate and thiocyanate.[18] Diels Alder reaction of maleic anhydride with 1,3-diene is used for the synthesis of substituted succinic anhydride and has been accelerated by microwaves.[19,20] In view of the importance of this functionality, and the suitability of microwave applications in its synthesis, we synthesized the substituted succinic anhydrides and used them in the synthesis of the imides. In this paper we wish to report two microwave assisted novel methods of synthesizing unsubstituted cyclic imides.

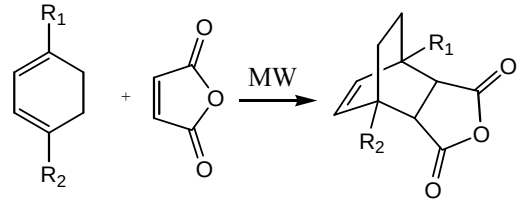
RESULTS AND DISCUSSION

Unsubstituted cyclic imides were synthesized by two methods under microwave irradiation. The first method uses cyclic anhydrides, NH_4Cl, and DMAP, while the second method uses the anhydrides with NH_4OAc, where both were found to be efficient (Scheme 1).



Scheme 1: Reaction of anhydrides with NH_4Cl / DMAP or NH_4OAc under Microwave Heating

The anhydrides used were either obtained commercially or synthesized through a microwave assisted Diels-Alder reaction of maleic anhydride and 1,3-cyclohexadienes, (α–terpinene, and cyclohexadiene) in both the mono-mode and conventional microwave ovens (Scheme 2).

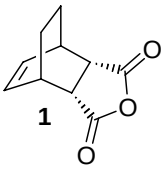
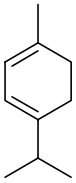
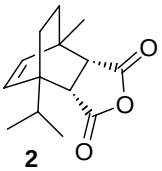


Scheme 2. Diels-Alder Reaction of 1,3-dienes with Maleic Anhydride

Maleic anhydride and the diene were mixed in a 1:1 molar ratio in solventless conditions and heated in a mono-mode microwave for 5 minutes at 150 ^{o}C. These substituted succinic anhydrides were isolated in good to excellent yields. Comparable results were obtained for the synthesis in a conventional microwave oven for 1 minute. The results are presented in Table 1 (Entries 1 and 2). The reactions were stereoselective with excellent endo selectivity as shown in Table 1. The stereoselectivity was determined

by Gas Chromatography and NMR. Purification of the endo products can be achieved by flash column chromatography.

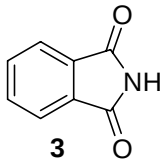
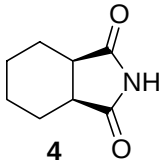
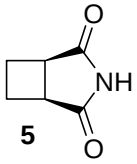
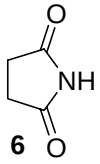
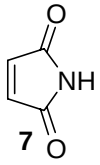
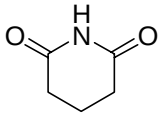
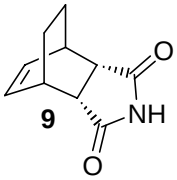
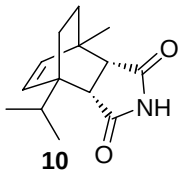
Table 1. Diels-Alder Reaction of Maleic Anhydride and 1,3-Cyclohexadiene

Entry	Diene	Anhydride	Mono mode			Conventional		
			endo / exo	Time-(min)	(%) Yield	endo / exo	Time-(min)	(%) Yield
1		 **1**	8 / 1	5	63	8 / 1	1	72
2		 **2**	13 / 1	5	82	15 /1	1	92

The precursor anhydrides of the listed cyclic imides (**3-10**) found in Table 2, were reacted with a mixture of ammonium chloride with 10% mole equivalents of DMAP used as a catalytic base. The mixture was heated in a mono-mode microwave for 5 minutes at 150 ^{o}C to give the products after flash chromatography with yields 61-90%. No reaction was observed when NH_4Cl was used without the addition of DMAP as the base. The solids did not melt after irradiating in the conventional microwave for 5 minutes. Alternatively, the imides were synthesized as shown in Table 2 from the corresponding anhydrides and NH_4OAc. Ammonium acetate when heated in the microwave seems to decompose into ammonia gas and acetic acid,[21]allowing for the reaction of ammonia gas with the anhydrides. Alternately these syntheses were also carried out in a conventional microwave for 2-5 minutes. Reaction completeness was determined in the conventional microwave through visually inspection of liquefaction and gas evolution in the reaction vessel. Imide (**5**) was properly identified and its single X-Ray structure was determined.[22]

The reactions of phthalic anhydride with NH_4Cl/DMAP or NH_4OAc under conventional heating were attempted neat. Heating in an oil bath at 150 ^{o}C gave no appreciable amount of products after 1 hour. The reactions were attempted in refluxing toluene, no product was obtained with the former, while 15% yield was obtained with NH_4OAc. This clearly shows the efficacy of microwave heating in this system. Maleic anhydride seemed to polymerize into an unidentifiable product that was not isolable. Although maleic anhydride did not react favorably, substituted succinic anhydrides were able to form the desired products indicating that the double bond reacts leading to byproduct formation for this reaction.

Table 2. Cyclic Imide Syntheses from (NH_4Cl/DMAP) and NH_4OAc in the CEM Discover

		NH_4Cl / DMAP				NH_4OAc			
		Mono.		Conv.		Mono.		Conv.	
Entry	Imide	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	Time (sec)	Yield (%)
1	 **3**	5	91	4	81	5	81	45	50
2	 **4**	5	81	4	69	5	51	45	90
3	 **5**	5	91	5	81	5	71	100	78
4	 **6**	5	91	5	69	5	81	45	73
5	 **7**	5	N.A.	-----		5	N.A.	------	
6	 **8**	5	81	2	90	5	53	15	92
7	 **9**	5	91	5	82	5	91	60	98
8	 **10**	5	~5	4	~5	5	40	240	72

This reaction is not suitable for a one pot reaction due to the reactivity of maleic anhydride indicated, while a two step one pot synthesis is possible where maleic anhydride is reacted first with the diene, then addition of the imidating reagents and irradiate again. The synthesis of **10** gave better yields with the

NH_4OAc reaction than that of the (NH_4Cl/DMAP) reaction. The possible cause of lower yields may be attributed to steric hindrance around the reaction centers and the ease of NH_4OAc decomposition. Monitoring the temperature of the reaction in the mono-mode microwave showed that the temperature of the mixture rises very slowly beyond room temperature to about 60 ^oC and suddenly increases to more than 150 ^oC when the mixture melts. The pressure also rises rapidly indicating the releasing of gases such as ammonia and HCl into the reaction vessel. The reaction temperature was set slightly above the highest melting point temperature of all given anhydrides to insure proper mixing.

Our methods seemed to be efficient as compared to previously reported synthesis time of imides (**9**) and (**10**) as they were obtained in quantitative yields (Diels-Alder reaction of maleimide and the corresponding diene in refluxing toluene for 4 days).[25]

Based on the results described above, we can conclude that the microwave-assisted reactions of the cyclic anhydrides with NH_4OAc or NH_4Cl/DMAP provide efficient general methods for the synthesis of *N*-unsubstituted cyclic imides in the mono-mode and conventional microwaves in minutes. The process is simple, gives high yields, and is suitable for scale up.

EXPERIMENTAL

General: The monomode microwave reactions were carried out in both a CEM Discover Microwave. Conventional microwave reactions were done in a Kennmore Microwave Oven (Household) Output: 1100 Watts (Frequency: 2450 MHz). All Gas Chromatograph Mass Spectrometry (GC-MS) were performed using a Shimadzu GC-17A and GCMS-QP5050A labsolutions system. All IR spectra were performed on a Perkin-Elmer Spectrum RX I FTIR system. All melting points determinations were performed on a Laboratory Devices Mel-Temp II instrument. All ^1H and ^{13}C-NMR spectra were recorded on a Bruker Avance spectrometer at 400 and 100 MHz respectively in $CDCl_3$ and DMSO-d_6. Chemical shifts are reported in δ (ppm), using TMS as internal standard. The assignment of ^{13}C-NMR spectra was supported by DEPT experiments. All solvents (HPLC grade) were purchased from Fisher Scientific Corporation. All reagents were purchased from Aldrich Chemical Company and were used without further purification. Method 1 corresponds to the mono-mode synthesis. Method 2 corresponds to the conventional synthesis. General procedures for NH_4OAc reaction in the microwave were similar to those of the NH_4Cl/DMAP methods. The imides synthesized are known compounds, either commercially available from Aldrich or reported earlier.

General procedure for Diels-Alder reaction in the microwave:

(Method 1)

endo-**Bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride** (**1**): 1,3-Cyclohexadiene (0.10 g, 1.24 mmol)

and maleic anhydride (0.12 g, 1.24 mmol) were thoroughly mixed in a CEM vial with a stirrer. This was capped and heated in a CEM Discover microwave for 5 min at 150 °C. This was rapidly cooled to rt yielding a white solid. The material was purified with a silica column (10 g) using EtOAc : Acetone (1:1) affording a white solid (0.14 g, 63%), mp 140–142 °C. [144-147 °C[23]]; ^{1}H-NMR (400 MHz) in $CDCl_3$: δ (ppm) = 6.30 (dd, J = 3.0, 4.5 Hz, 2H), 3.17 (m, 2H), 1.61 (m, 4H), 1.39 (bd, J = 7.5 Hz, 4H), ^{13}C-NMR (100 MHz) in $CDCl_3$: δ (ppm) = 173.89 (C=O), 13282 (CH), 44.53 (CH), 31.42 (CH), 22.69 (CH2). MS m/z:178 (M+) 106, 91, 78, 50; IR ($CHCl_3$) (νmax, cm^{-1}): 1715.5, 1780.9 (C=O).

Method 2

1-Isopropyl-4-methyl-endo-bicyclo[2.2.2]oct-5-ene-2,3-dicarboxylic anhydride (2)[24]: α-Terpenine (1.0 g, 7.33 mmol) and maleic anhydride (0.72 g, 7.34 mmol) were mixed in a loosely tightened 8 mL teflon capped vial. The sample was allowed to heat for 1 min at full power and then cooled to rt. This was purified on a silica gel column (30 g) using EtOAc : hexanes (1:1) yielding a white solid (1.60 g, 92%), mp 50-52 °C; ^{1}H-NMR (400 MHz) ($CDCl_3$): δ (ppm) = 6.067 (d, J = 8.5 Hz, 1H), 6.014 (d, J = 8.5 Hz, 1H), 3.80 (d, J = 6.5 Hz, 2H), 3.28 (d, J = 8.5, 1H), 2.91 (d, J = 8.5 , 1H), 2.51 (septet , J = 6.8 Hz, 1H), 1.52 (m, 1H), 1.45 (s, 3H), 1.32 (m, 1H), 1.031 (d, J = 6.8Hz , 3H), 0.958 (d, J = 6.9Hz, 3H); ^{13}C-NMR (100 MHz) in $CDCl_3$: δ (ppm) = 171.47 (C=O), 170.84 (C=O), 136.64 (CH), 135.89 (CH), 50.52 (CH), 47.85 (CH), 43.09 (C), 36.26 (C), 33.12 (CH_2), 29.00 (C), 22.24 (CH_2), 21.75 (CH_3), 17.90 (CH_3), 16.26 (CH_3); MS m/z: 234 (M+) 163, 135, 119, 91; IR ($CHCl_3$) (νmax, cm^{-1}): 1770.6, 1834.2 (C=O).

General procedure for (NH_4Cl/ DMAP) reaction in the microwave:

Method 1

Phthalimide (**3**): Phthalic anhydride (0.10 g, 0.675 mmol), ammonium chloride (0.036 g, 0.675 mmol), and DMAP (0.04 g, 0.34 mmol) were thoroughly mixed in a CEM vial with a stirrer. This was capped and heated in a CEM Discover microwave for 5 min at 150 °C. This was rapidly cooled to rt. yielding a dark brown solid. The material was dissolved in 4 mL of EtOAc and was washed with (2x) 2mL of distilled water. The organic layer was dried to afford a white solid (0.09 g, 91%).

Method 2

Phthalimide (**3**): Phthalic anhydride (1.0 g, 6.75 mmol), DMAP (0.17 g, 1.4 mmol), and NH_4Cl (0.42 g, 7.85 mmol) were mixed in an 8 mL Teflon capped vial. The sample was allowed to heat for 4 min and 11 sec. at 30 percent power and then cooled to rt. This was purified on a short column (30 g) with pure acetone. The organic layer was concentrated affording a yellow solid (0.80 g, 81%).

Phthalimide (**3**): White solid, mp 226-228 °C [232-235 °C[23]]; ^{1}H-NMR (400MHz) in $CDCl_3$: δ (ppm) = 7.88 (m, 2H), 7.77 (m, 2H), 7.71 (bs, 1H, NH): ^{13}C-NMR (100 MHz) in DMSO-d6): δ (ppm) = 169.07 (C=O), 134.07 (CH), 132.56 (C), 122.77 (CH); MS m/z: 147 (M +) 104, 76, 50; IR ($CHCl_3$) (νmax, cm^{-1}): 1739.7, 1776.8 (C=O).

3a,4,5,6,7,7a-Hexahydro-1*H*-isoindole-1,3(2*H*)-dione (**4**): White solid, mp 131-133 °C [134.5–135 °C[25]]; ^{1}H-NMR (400MHz) in $CDCl_3$: δ (ppm) = 9.525 (bs,1H, NH), 2.924 (m, 2H), 1.83 (m, 4H), 1.47 (m, 4H); ^{13}C-NMR (100 MHz) in $CDCl_3$: δ (ppm) = 180.867 (C=O), 40.73 (CH), 23.45 (CH_2), 21.44 (CH_2); MS m/z: 153 (M+) 125, 99, 82, 67, 54, 41; IR ($CHCl_3$) (νmax, cm^{-1}): 1720.4, 1781.6 (C=O).

***cis*-1,2-Cyclobutanedicarboximide** (**5**)**:** White crystals from MeOH, mp 135-137 °C [mp 137.5–138 °C[25]]; ^{1}H-NMR (400 MHz) ($CDCl_3$): δ (ppm) = 9.49 (bs, 1H, NH), 3.324 (m, 2H), 2.687 (m, 2H), 2.273 (m, 2H); ^{13}C-NMR (100 MHz) in $CDCl_3$: δ (ppm) = 181.49 (C=O), 39.77 (CH), 22.04 (CH_2); MS m/z: 125 (M+), 82, 54; IR ($CHCl_3$) (νmax, cm^{-1}): 1723.8, 1781.2 (C=O).

Succinimide (**6**)**:** White solid, mp 122-124 °C [123-125 °C[23]]; ^{1}H-NMR (400MHz) in $CDCl_3$: δ (ppm) = 8.98 (bs, 1H, NH), 2.76 (s, 4H); ^{13}C-NMR (100 MHz) in $CDCl_3$: δ (ppm) = 178.07 (C=O), 29.57 (CH_2); MS m/z: 99 (M +) 56; IR ($CHCl_3$) (ν_{max}, cm^{-1}): 1711.0 (C=O).

Glutarimide (**8**)**:** White solid, mp 154-156 °C [155-157 °C[23]]; 1H-NMR (400MHz) in $CDCl_3$: δ (ppm) = 9.06 (bs, 1 H, NH), 2.59 (t, J = 6.6 Hz, 4H), 2.02 (quintet, J = 6.6Hz, 2H); ^{13}C-NMR (100 MHz) in $CDCl_3$: δ (ppm) = 173.45 (C=O), 32.43 (CH_2), 17.68 (CH_2); MS m/z 113 (M+), 70, 42; IR ($CHCl_3$) (νmax, cm^{-1}): 1710.0, 1795.0 (C=O).

3a,4,7,7a-Tetrahydro-4,7-ethano-1*H*-isoindole-1,3(2*H*)-dione (**9**)[26]**:** White solid, mp 200-202 °C; ^{1}H-NMR (400 MHz) in $CDCl_3$: δ (ppm.) = 849 (bs, 1H, NH), 6.23 (dd J= 3.0, 4.5 Hz, 2H), 3.14 (m, 2H), 2.88 (m, 2H), 1.58 (bd, J = 7.5 Hz, 2H), 1.14 (bd, J = 7.5 Hz, 2H), ^{13}C-NMR (100 MHz) in $CDCl_3$: δ (ppm) = 179.39 (C=O), 132.30 (CH), 45.53 (CH), 31.57 (CH), 23.46 (CH_2); MS m/z: 177 (M+) 149, 99, 78, 51; IR ($CHCl_3$) (νmax, cm^{-1}): 1714.68, 1784.61 (C=O), 3019.60.

3a,4,7,7a-Tetrahydro-4-isopropyl-7-methyl-4,7-Ethano-1*H*-isoindole-1,3(2*H*)-dione (**10**)[25]: White solid, mp 138-140 °C;. ^{1}H-NMR (400 MHz) in $CDCl_3$: δ (ppm) = 8.04 (bs, 1H, NH), 6.067 (d, J = 8.3 Hz, 1H), 5.94 (d, J = 8.3 Hz, 1H), 2.99 (d, J = 7.5 Hz, 1H), 2.59 (m, 2H), 1.47 (s, 3H), 1.4-1.2 (m, 2H) 1.07 (d,

J = 6.5 Hz, 3H), 1.0-0.8 (m, 2H), 0.98 (d, J = 6.5 Hz, 3H): ^{13}C-NMR (100 MHz) in $CDCl_3$: δ (ppm) = 177.98 (C=O), 177.57 (C=O), 136.31 (CH), 135.60 (CH), 51.57 (CH), 47.73 (CH), 43.51 (C), 36.74 (C), 34.24 (CH_2), 29.47 (CH), 22.85 (CH_2), 22.51 (CH_3), 18.36 (CH_3), 16.82 (CH_3); MS m/z: 233 (M +) 163, 135, 119, 91; IR ($CHCl_3$) (νmax, cm^{-1}): 1709.2, 1761.4 (C=O), 3018.6.

ACKNOWLEDGEMENTS

We thank NIH for support through research centers in minorities institutions (RCMI) grant # 5 G12 RR017581.

REFERENCES

1. J. Bauer and J. Rademann, *Tetrahedron Lett.,* 2003, **44**, 5019; A. DaSettimo, G. Primofiore, F. Da Settimo, F. Simorini, C. LaMotta, A. Martinelli, S. E. Mallakpour, A.-R. Hajipour, and S. Habibi, *Eur. Polym. J.,* 2001, **37**, 2435; S. E. Mallakpour, A. R. Hajipour, K. Faghihi, N. Foroughifar, and J. Bagheri, *J. Appl. Polym. Sci.,* 2001, **80**, 2416.
2. Q. Zhou, X. Jiang, X. Shao, G. J. Chen, M. X. Jia, and Z. T. Li, *Org. Lett.,* 2003, **5**, 1955; J. He, K. Horie, R. Yokota, and F. He, *Polymer,* 2001, **42**, 4063; D. J. Liaw and B. Y. Liaw, *Polymer,* 2001, **42**, 839.
3. A. I. Meyers, B. A. Lefker, T. J. Sowin, and L. J. Westrum, *J. Org. Chem*., 1989, **54**, 4243; B. Martin, H. Sekljic, and C. Chassaing, *Org. Lett.,* 2003, **5**, 1851; N. Flaih, C. Pham-Huy, and H. Galons, *Tetrahedron Lett.,* 1999, **40**, 3697; T. Vidal, A. Petit, A. Loupy, and R. N. Gedye, *Tetrahedron*, 2000, **56**, 5473; A. K. Bose, M. S. Manhas, M. Ghosh, V. S. Raju, K. Tabei, and Z. Urbanczyk-Lipkowska, *Heterocycles,* 1990, **30**, 741; A. K. Bose, *Org. Synth. Coll. Vol.,* 1973, **5**, 973.
4. P. Y. Reddy, S. Kondo, T. Toru, and Y. Ueno, *J. Org. Chem.,* 1997, **62**, 2652 and references therein.; P. Garner, W. B. Ho, S. K. Grandhee, W. J. Youngs, and V. O. Kennedy, *J. Org. Chem*., 1991, **56,** 5893.
5. T. Polonaski, M. J. Milewska, and M. Gdaniec, *Tetrahedron: Asymmetry,* 2000, **11**, 3113.
6. G. W. Muller, W. E. Konnecke, A. M. Smith, and V. D. Khetani, *Org. Process Res. Dev.,* 1999, **3,** 139.
7. A. J. Gordon and R. L. E. Ehrenkaufer, *J. Org. Chem.,* 1971**, 36**, 44.
8. E. Bon, R. Reau, G. Bertand, and D. C. H. Bigg, *Tetrahedron Lett.,* 1996, **37**, 1217.
9. G. J.Handley, E. R. Nelson, and T. C. Somers, *Australian J. Chem.,* 1960, **13**, 127.
10. E. W. Ganin, W. F. Makarow, and W. I. Nukitin, *Z. Org. Khim.,* 1987, **23**, 1086.

11. P. Lidstrom, J. Tierney, B. Wathey, and J. Westman, *Tetrahedron,* 2001, **57**, 9225.
12. S. Chandrasekhar, M. B. Padmaja, and A. Raza, *Synlett*, 1999, 1597.
13. H. N. Borah, R. C. Boruah, and J. S. Sandhu, *J. Chem. Res. (S),* 1998, 272.
14. Y. Xu and Q.-X. Guo, *Heterocycles*, 2004, **63**, 903.
15. J. A. Seijas, P. Vazquez-Tato, M. Montserrat-Martinez, and G. J. Nŭnez-Corredoira, J. *Chem. Res.* **(S),**1999, 420; J. A. Seijas, M. P. Vázquez-Tato, C. González-Bande, M. M. Martínez, and B. Pacios-López, *Synthesis,* 2001*,* **7***,* 999.
16. Y. Peng, G. Song, and X. Qian, *Synth. Commun*., 2001, **31**, 1927; K. Kacprzak*, Synth. Commun.,* 2003*,* **33**, 1499.
17. G. Bratulescu, *Revista de Chimie (Bucharest)*, 2000, **51**, 167.
18. F. Nikpour, S. Kazemi, and D. Sheikh, *Heterocycles,* 2006, **68**, 1559.
19. B. Garrigues, C. Laporte, R. Laurent, A. Laporterie, and J. Dubac, *Liebigs Ann.*, 1996, 739.
20. A. K. Bose, M. S. Manhas, M. G. Ghosh, M. Shah, V. S. Raju, S. S. Bari, S. N. Newaz, B. K. Banik, A. G. Chaudhary, and K. J. Barakat, *J. Org. Chem*., 1991, **56**, 6968.
21. Y. Xu, L.-F. Wan, H. Salehi, W. Deng, and Q.-X. Guo, *Heterocycles,* 2004, **63**, 1613.
22. R. J. Butcher, Y. M. Hijji, and E. Benjamin, *Acta Cryst.,* 2006, **E62**, o1266.
23. Data from Aldrich Chemical Company (Commerically available)
24. A. Weisz and A. Mandelbaum, *J. Org. Chem.*, 1988, **53**, 5812.
25. G. C. Crockett and T. H. Koch*, J. Org. Chem.*, 1977, **42**, 2721.
26. G. Sastre, A. Cantin, M. J. Diaz-Cabanãs, and A. Corma, *Chem. Mater.,* 2005, **17**, 545.