International Journal of Organic Chemistry, **2013, 3, 275-279**
Published Online December 2013 (http://www.scirp.org/journal/ijoc)
http://dx.doi.org/10.4236/ijoc.2013.34039

Solvent-Free Synthesis of 5-Alkenyl-2,2-butylidene-1, 3-dioxane-4,6-diones under Ultrasonic Irradiation with o-Phthalimide-N-Sulfonic Acid as Catalyst

Chunhua Lin, Zhaohui Xu, Weilin Liao
Fine Chemical Key Laboratory of Jiangxi Province, Nanchang, China
Email: gotoxzh@163.om, liao1liao2@163.com

Received October 20, 2013; revised November 25, 2013; accepted December 11, 2013

ABSTRACT

5-Alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones were synthesized by the Knoevenagel condensation reaction of aromatic aldehydes with 2,2-butylidene-1,3-dioxane-4,6-dione using o-phthalimide-N-sulfonic acid as catalyst, without solvent under ultrasonic irradiation. The present method has some notable advantages such as mild reaction conditions, short reaction times, less catalyst dosage and high yields with the green aspects by avoiding toxic catalysts and solvents. Further, the catalyst can be reused for five times without any noticeable decrease in the catalytic activity.

Keywords: o-Phthalimide-N-Sulfonicacid; 5-Alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones; Aromatic Aldehydes; Knoevenagel Condensation

1. Introduction

In recent years, the preparation of 5-alkenyl-1,3-dioxane-4,6-diones has attracted strong interest owing to the broad spectrum of their properties: these compounds can be employed as versatile intermediates for a series of natural products and heterocyclic compounds with potentially biological activity [1-5]. In addition, it is also reacted with Grignard reagent in conjugate addition [6] or conjugated dienes in Diels-Alder cycloaddition [7]. In particular, 5-alkenyl-2,2-dimethyl-1,3-dioxane-4,6-dione is an important reagent for synthesizing lipid-lowering drugs "Lipitor" [8]. Therefore, the preparation of 5-alkenyl-1,3-dioxane-4,6-diones is of much current importance.

More recently, lots of methods for the synthesis of 5-alkenyl-1,3-dioxane-4,6-diones have been reported in the literature. Generally, they were synthesized by the Knoevenagel condensation reaction of 1,3-dioxane-4,6-diones and aromatic aldehydes in the presence of bases such as pyridine [9,10], piperidine/glacial acetic acid [11, 12], or hexamethyldisilazane [13] and Lewis acids, such as anhydrous zinc chloride [14], $TiCl_4$/pyridine [15] and $CePW_{12}O_{40}$ [16]. However, many of these methodologies have not been entirely satisfactory, owing to such drawbacks as low yields, long reaction time, more catalyst dosage, environmentally unfavorable solvents, emerging the problems of tedious work-up and effluent pollution. Uncatalyzed reaction was also reported in the literature using DMF or DMSO as solvent, which is toxic, teratogenic and suspected carcinogen. Those methods gave mixtures of unsaturated and Michael addition products [17]. Thus, a mild, efficient, and environmentally friendly method using economical catalyst is desirable.

Recently, the solvent-free condition and the use of heterogeneous catalysts have emerged as an eco-friendly alternative of great importance within organic synthesis, as they reduce environmental pollution and bring down handling costs due to simplification of work-up technique [18].

Ultrasound has increasingly been used in organic synthesis in the last three decades. Compared with traditional methods, the procedure is more convenient and can be carried out in higher yields, shorter reaction time or milder conditions under ultrasound irradiation [19-23]. Our investigations on the application of ultrasound in organic synthesis [16] and our work on Knoevengel condensations [13,24] are continued. Herein, we would like to report an efficient and practical procedure for the synthesis of 5-alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones with 2,2-butylidene-1,3-dioxane-4,6-dione [23,25] and

aromatic aldehydes in o-phthalimide-N-sulfonic acid (OPNSA) without solvent under ultrasound irradiation (**Scheme 1**).

2. Results and Discussion

To optimize the reaction conditions, a selected model reaction was carried out with 2,2-butylidene-1,3-dioxane-4,6-dione **1** (0.01 mol, 1.7 g), benzaldehyde **2** (0.01 mol) and different sets of reaction conditions. The results are summarized in **Table 1**. The results clearly show that the catalyst is essential, the catalytic activity of o-phthalimide-N-sulfonic acid (OPNSA) is high, giving **3a** in high yield in a short reaction time. Using OPNSA as the catalyst, we evaluated the reaction in various solvents and under solvent-free conditions. The product yield in a polar solvent was higher than the one in non-polar solvent, but under solvent-free conditions the highest yield was obtained (**Table 1**, **Entries 1-8**). The catalyst (OPNSA) plays a crucial role in the success of the reaction in terms of the yields. The presence of 0 mol% OPNSA gave the product **3a** in quantitative yield (35%) at 60˚C. Increasing the catalyst to 1, 3, and 5 mol% results in improved reaction yields to 76%, 89% and 87% respectively (**Table 1, Entries 8-11**). Use of just 3 mol% OPNSA is sufficient to push the reaction forward. Higher amounts of the catalyst did not improve the results to a great extent. Thus, 3 mol% OPNSA was chosen as a quantitative catalyst for these reactions.

To find the optimum reaction time, the reaction was carried out in the presence of OPNSA for 20, 30, 40 and 60 minutes, resulting in the isolation of **3a** in 90%, 91%, 90% and 89% yield, respectively. Similarly, the optimum reaction temperature was 30˚C. In addition, it must be pointed out that all of these reactions were carried out without solvent under ultrasonic irradiation. Under mechanical agitation conditions the product yield for 68% and with ultrasonic irradiation the product yield for 91%, which indicated the ultrasonic radiation to promote the reaction effectively (**Table 1**, **Entries 16**, **17**). The best results was obtained when was conducted at 30˚C, for 30 minutes in the presence of 3 mol% OPNSA (**Table 1**, **Entry 16**).

To determine the generality of this method, the scope of the reaction was investigated using a number of aromatic aldehydes under the optimized reaction conditions. The results are presented in **Table 2**. The results show benzaldehyde and aromatic aldehydes with electron with drawing groups (-Cl, -NO_2, -F) and electron-donating groups (-OCH_3, -OH, -$N(CH_3)_2$) have all provided high yields of the products.

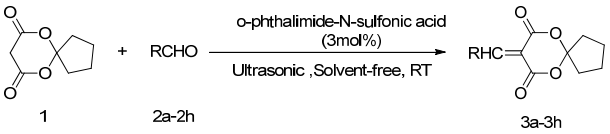
The principle advantages of the use of o-phthalimide-N-sulfonic acid (OPNSA) in organic transformations are their reusability. The catalyst was readily recovered from the reaction mixture using the procedure outlined in the experimental section. The separated catalyst was washed with 2-methoxy-2-methylpropane (10 mL), it was directly used in a similar reaction. From **Table 3** we found that the catalyst could be used at least five times with only a slight reduction in activity (91% yield for first use, 91% for second use, 90% for third use, 89% for fourth time and 86% for fifth time).

A plausible mechanism for the formation of the 5-alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones products using o-phthalimide-N-sulfonic acid (OPNSA) as a catalyst has been depicted in **Scheme 2**.

Table 1. Optimization of reaction conditions for synthesizing compound (3a)[a].

Entry	Solvent	Catalyst (mol%)	Temperature (˚C)	Time (min)	Yield[b] (%)	Experiment method
1	C_2H_5OH	3	Reflux	120	81	Ultrasonic
2	CH_3OH	3	Reflux	120	80	Ultrasonic
3	CH_3CN	3	Reflux	150	72	Ultrasonic
4	THF	3	Reflux	150	73	Ultrasonic
5	C_6H_6	3	Reflux	180	66	Ultrasonic
6	CH_2Cl_2	3	Reflux	210	68	Ultrasonic
7	H_2O	3	Reflux	120	78	Ultrasonic
8	None	3	60	60	89	Ultrasonic
9	None	5	60	60	87	Ultrasonic
10	None	1	60	60	76	Ultrasonic
11	None	0	60	120	35	Ultrasonic
12	None	0	60	120	24	Mechanical
13	None	3	50	60	89	Ultrasonic
14	None	3	40	40	90	Ultrasonic
15	None	3	30	30	91	Ultrasonic
16	None	3	30	20	90	Ultrasonic
17	None	3	30	60	68	Mechanical

[a]Reaction conditions: benzaldhyde (0.01 mol), 2,2-butylidene-1,3-dioxane-4,6-dione (1.70 g, 0.01 mol), solvent (10 mL) or solvent-free conditions (power ultrasonic irradiation 250 W, irradiation frequency 40 kHz); [b]Isolated yields.



Scheme 1. Synthesis of 5-alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones.

Table 2. OPNSA-catalyzed synthesis of 5-alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones (3a-3h)[a].

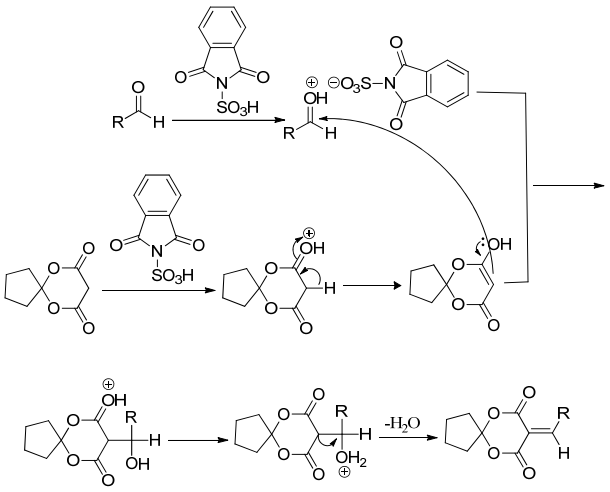
R	Product	Time (min)	Yield[b] (%)	Melting point(℃)	
				Found	Reported [Ref.]
C_6H_5	3a	30	91	87 - 88	88 - 90 [26]
4-HO-C_6H_4	3b	35	88	170 - 172	170 - 172 [26]
4-CH_3O-C_6H_4	3c	35	89	83 - 85	83 - 85 [16]
4-NO_2-C_6H_4	3d	15	93	150 - 152	150 - 152 [16]
2-NO_2-C_6H_4	3e	20	91	112 - 114	113 - 115 [16]
4-F-C_6H_4	3f	15	87	86 - 88	86 - 88 [26]
4-Cl-C_6H_4	3g	20	84	115 - 116	114 - 116 [16]
4-$(CH_3)_2N$-C_6H_4	3h	25	92	180 - 182	180.5 - 181 [16]

[a]Reaction conditions: benzaldhyde (0.01 mol), 2,2-butylidene-1,3-dioxane-4,6-dione (1.70 g, 0.01 mol), OPNSA catalyst (3 mol%), 30˚C, solvent-free conditions (power ultrasonic irradiation 250 W, irradiation frequency 40 kHz); [b]Isolated yields.

Table 3. The recycling of OPNSA in synthesis of 3a under the reaction optimized conditions.

Entry	Time (min)	Yield[a] (%)
1	30	91
2	35	91
3	35	90
4	38	89
5	40	86

[a]Isolated yields.



Scheme 2. The plausible mechanism for synthesis of the 5-alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones.

3. Conclusion

The catalyst of o-phthalimide-N-sulfonic acid (OPNSA), showed high catalytic activity in the synthesis of 5-alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones synthesized by the Knoevenagel condensation reaction of aromatic aldehydes with 2,2-butylidene-1,3-dioxane-4,6-dione without solvent under ultrasonic irradiation. This procedure offers several advantages over the other techniques available in the literature, including much shorter reaction times, higher yields, milder conditions, and the absence of any hazardous organic solvents, which makes it a useful and attractive protocol for the synthesis of these compounds. Furthermore, the catalyst could be recycled after a simple work-up, and used at least five times without significant reduction in its catalytic activity.

4. Experimental Section

4.1. Reagents and Instruments

All chemicals were purchased from Aladdin, Aldrich and Fluka Chemical Companies and without further purification. The melting points of the various compounds were measured by XT-4 digital micro melting point instrument and are uncorrected. Reaction monitoring was accompanied by TLC using silica gelSIL G/UV 254 plates. KQ-250E-machine ultrasonic instrument is made in Kunshan Co., LTD. IR spectra were taken on a Nicolet-360 FT-IR spectrometer by incorporating samples in KBr disks. ^{1}HNMR spectra were recorded with Bruker Avance 400 MHz spectrometer with $CDCl_3$ as the solvent and TMS as the internal standard. The ^{13}CNMR data were collected on Bruker Avance 100 MHz instrument with $CDCl_3$ as the solvent and TMS as the internal standard.

4.2. Preparation of o-Phthalimide-N-Sulfonic Acid (OPNSA)

A solution of chlorosulfonic acid (11.6 g, 0.1 mol) in CH_2Cl_2 (20 ml) was added to o-Phthalimide (14.7 g, 0.1 mol) in CH_2Cl_2 (20 ml) solution at 0˚C. Then the mixture was stirred at room temperature for 24 h. The solvent was evaporated at reduced pressure and the remaining solid was washed with 2-methoxy-2-methylpropane (3 × 10 mL) and filtered to give the desired product as a yellow solid material in 97% yield.

4.3. General Procedure for Synthesis of 5-Alkenyl-2,2-butylidene-1,3-dioxane-4,6-diones

2,2-butylidene-1,3-dioxane-4,6-dione **1** (0.01 mol, 1.7 g), aromatic aldehyde **2** (**2a-2h**, 0.01 mol) and o-phthalimide-N-sulfonic acid (OPNSA) 3 mol% were taken in a round bottom flask, then the mixture was stirred under ultrasound irradiation at room temperature for 15 - 35 min. Upon completion of the reaction, as confirmed by thin-layer chromatography (petroleum ether/ethyl acetate

5:1), the reaction mixture was diluted with 20 mL ethanol. The catalyst was collected from the filtrate, which was concentrated on reduced pressure. After the remaining catalyst was washed with 2-methoxy-2-methylpropane (10 mL), it was directly used for the next reaction. The crude solid product was filtered and then purified by recrytallization from ethanol to afford the pure product **3** (**3a-3h**). The physical data (mp, IR, NMR) of known compounds were identical to the corresponding literature data.

4.4. The Data for Representative Compounds

5-*Benzylidene*-2,2-*butylidene*-1,3-*dioxane*-4,6-*dione* (Compound 3a, **Table 1**): White solid (yield: 91%), M.p. 87˚C - 88˚C; IR ν_{max} (KBr): 2951, 1763, 1734, 1626, 1571, 741,693 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.37 (s, 1H), 8.02 (d, J = 7.14 Hz, 2H), 7.56 - 7.47 (m, 3H), 2.22 (s, 4H), 1.89 (s, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ163.86, 160.48, 157.65, 133.65, 133.49, 131.68, 128.76, 115.71, 113.75, 38.54, 23.28.

5-(4-*Hydroxybenzylidene*)-2,2-*butylidene*-1,3-*dioxane*-4,6-*dione* (Compound 3b, **Table 1**): White solid (yield: 88%), M.p. 170˚C - 172˚C; IR ν_{max} (KBr): 2965, 2957, 1750, 1700, 1638, 1537, 1400, 1170, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.35 (s, 1H), 8.12 (d, J = 8.82 Hz, 2H), 6.94 (d, J = 8.82 Hz, 2H), 2.24 - 2.19 (m, 4H), 1.90 - 1.85 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz,): δ 164.93, 162.17, 158.37, 137.88, 124.43, 116.21, 113.67, 110.94, 38.41, 23.26.

5-(4-*Methoxybenzylidene*)-2,2-*butylidene*-1,3-*dioxane*-4,6-*dione* (Compound 3c, **Table 1**): White solid (yield: 89%), M.p. 83˚C - 85˚C; IR ν_{max} (KBr): 2972, 2901, 1756, 1718, 1624, 1573, 1455, 1381, 1183, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.32 (s, 1H),8.19 (d, J = 8.97 Hz, 2H), 6.98 (d, J = 8.97 Hz, 2H), 3.90 (s, 3H), 2.23 - 2.18 (m, 4H), 1.90 - 1.85 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz,): δ 164.62, 161.19, 157.56, 137.48, 124.71, 114.38, 113.37, 111.65, 55.68, 38.41, 23.26.

5-(4-*Nitrobenzylidene*)-2,2-*butylidene*-1,3-*dioxane*-4,6-*dione* (Compound 3d, **Table 1**): Pale yellow solid (yield: 93%), M.p. 150˚C - 152˚C; IR ν_{max} (KBr): 2976, 2901, 1763, 1731, 1626, 1605, 1524, 1350, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.41 (s, 1H), 8.30 (d, J = 8.82 Hz, 2H), 8.06 (d, J = 8.70 Hz, 2H), 2.27 - 2.23 (m, 4H), 1.95 - 1.90 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 162.36, 159.36, 153.67, 149.26, 137.11, 132.73, 123.30, 119.17, 114.08, 36.43, 23.00.

5-(2-*Nitrobenzylidene*)-2,2-*butylidene*-1,3-*dioxane*-4,6-*dione* (Compound 3e, **Table 1**): Pale yellow solid (yield: 91%), M.p. 112˚C - 114˚C; IR ν_{max} (KBr): 2963, 2908, 1765, 1736, 1625, 1604, 1524, 1363, 800 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.75 (s, 1H), 8.28 (d, J = 8.22 Hz, 1H), 7.78 - 7.62 (m, 2H), 7.49 (d, J = 7.56 Hz, 1H), 2.24 - 2.21 (m, 4H), 1.91 - 1.89 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz): δ 161.69, 159.22, 155.09, 145.99, 133.46, 130.57, 129.99, 129.39, 124.44, 118.19, 114.14, 38.23, 22.87.

5-(4-*Furylmethylene*)-2,2-*butylidene*-1,3-*dioxane*-4,6-*dione* (Compound 3e, **Table 1**): White solid (yield: 87%), M.p. 86˚C - 88˚C; IR ν_{max} (KBr): 2961, 2943, 1757, 1726, 1598, 1604, 1508, 1364, 1081, 840, 804 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.33 (s, 1H), 8.14 (d, J = 5.58, 8.64 Hz, 2H), 7.16 (t, J = 8.61 Hz, 1H), 2.24 - 2.19 (m, 4H), 1.91 - 1.86 (m, 4H); ^{13}CNMR ($CDCl_3$, 100 MHz,): δ 167.44, 164.01, 163.81, 160.54, 156.21, 136.73, 136.60, 128.07, 128.03, 116.27, 115.98, 114.99, 114.96, 113.74, 38.49, 23.24.

5. Acknowledgements

The authors thank the financial support from the National Science and Technology Project (No. 2001BA323C) and the Graduate Innovation Foundation of Jiangxi Province (No.YC10A051).

REFERENCES

[1] R. T. Acobs, A. D. Wright and F. X. Smith, "Condensation of Monosubstituted Isopropylidene Malonates with Mannich Bases," *Journal of Organic Chemistry*, Vol. 47, No. 19, 1982, pp. 3769-3772. http://dx.doi.org/10.1021/jo00140a038

[2] R. Bruns, A. Wernicke and P. Koll, "Application of the Reaction of D-Glucose with Meldrum's Acid: Total Synthesis of the Styryl Lactones (+)-Goniofufurone and (+)-7-epi-goniofufurone," *Tetrahedron*, Vol. 55, No. 32, 1999, pp. 9793-9800.

[3] I. N. Nestrova, A. K. Shanazarov and A. M. Poznyak, "Improved Method of Synthesis 2,2-Dimethyl-4,6-dioxo-1,3-dioxane (Meldrum's Acid)," *Pharmaceutical Chemistry Journal*, Vol. 28, No. 8, 1994, pp. 583-585. http://dx.doi.org/10.1007/BF02219035

[4] E. M. Abdelaziz, A. C. Jhonny Azuaje, C. Ernesto, Y. C. Matilde, Y. C. Vicente and S. Eddy, "Discovery and Preliminary SAR of 5-Arylidene-2,2-dimethyl-1,3-dioxane-4,6-diones as Platelet Aggregation Inhibitors," *Combinatorial Chemistry & High Throughput Screening*, Vol. 15, No. 7, 2012, pp. 551-554. http://dx.doi.org/10.2174/138620712801619122

[5] W. G. Rajecwarna, R. B. Labroo and L. A. Cohen, "Synthesis of 5-[(Indol-2-on-3-yl)methyl]-2,2-dimethyl-1,3-dioxane-4,6-diones and Spirocyclopropyloxindole Derivatives. Potential Aldose Reductase Inhibitors," *Journal of Organic Chemistry*, Vol. 64, No. 4, 1999, pp. 1369-1371.

[6] T. Watanabe, T. F. Knpfel and E. M. Carreira, "Asymmetric Conjugate Addition Reactions of Meldrum's Acid Derived Acceptors Employing Chiral Phosphoramidite Ligands," *Organic Letters*, Vol. 5, No. 25, 2003, pp. 4557-4558. http://dx.doi.org/10.1021/ol035575q

[7] E. Fillion, A. M. Dumas and S. A. Hogg, "Modular,

Modular Synthesis of Tetrahydrofluorenones from 5-Alkylidene Meldrum's Acids," *The Journal of Organic Chemistry*, Vol. 71, No. 26, 2006, pp. 9899-9902. http://dx.doi.org/10.1021/jo0618876

[8] S. Rádl, J. Stach and J. Hajicek, "An Improved Synthesis of 1,1-Dimethylethyl6-cyanomethyl-2,2-dimethyl-1,3-dioxane-4-acetate, a Key Intermediate for Atorvastatin Synthesis," *Tetrahedron Letters*, Vol. 43, No. 11, 2002, pp. 2087-2090.

[9] D. Davidson and S. A. Bernhard, "The Structure of Meldrum's Supposed β-Lactonic Acid," *Journal of the American Chemical Society*, Vol. 70, No. 10, 1948, pp. 3426-3428. http://dx.doi.org/10.1021/ja01190a060

[10] E. J. Corey, "The Mechanism of the Decarboxylation of α,β- and β,γ-Unsaturated Malonic Acid Derivatives and the Course of Decarboxylative Condensation Reactions in Pyridine," *Journal of the American Chemical Society*, Vol. 74, 1952, pp. 5897-5905. http://dx.doi.org/10.1021/ja01143a021

[11] G. A. Kraus and M. E. Krolski, "Synthesis of a Precursor to Quassimarin," *Journal of Organic Chemistry*, Vol. 51, No. 17, 1986, pp. 3347-3450. http://dx.doi.org/10.1021/jo00367a017

[12] P. Scuster, O. E. Polansky and F. Wessely, "Zur Kenntnis cyclischer Acylale, 6. Mitt.," *Monatshefte für Chemie*, Vol. 95, 1964, pp. 53-58. http://dx.doi.org/10.1007/BF00909251

[13] Z. H. Xu, N. Yan and W. L. Liao, "Knoevenagel Condensation Reaction of 2,2-Dimethyl-1,3-dioxane-4,6-dione and Aromatic Aldehydes by Hexamethyldisilazane," *Chinese Journal of Jiangxi Normal University* (*Natural Science*), Vol. 36, No. 5, 2012, pp. 524-526.

[14] P. S. Rao and R. V. Venkataratnam, "Zinc Chloride as a New Catalyst for Knoevenagel Condensation," *Tetrahedron Letters*, Vol. 32, No. 41, 1991, pp. 5821-5822. http://dx.doi.org/10.1016/S0040-4039(00)93564-0

[15] A. M. Dumas and E. Fillion, "Meldrum's Acids and 5-Alkylidene Meldrum's Acids in Catalytic Carbon-Carbon Bond-Forming Processes," *Accounts of Chemical Research*, Vol. 43, No. 3, 2009, pp. 440-454. http://dx.doi.org/10.1021/ar900229z

[16] Z. H. Xu and C. H. L, "Solvent-Free Synthesis of 5-Alkenyl-2,2-pentamethylene-1,3-dioxane-4,6-diones under Ultrasonic Irradiation with $CePW_{12}O_{40}$ as Catalyst," *Chinese Journal of Organic Chemistry*, Vol. 33, No. 7, 2013, pp. 1540-1544.

[17] A. M. Dumas, A. Seed, A. K. Zorzitto and E. Fillion, "A General and Practical Preparation of Alkylidene Meldrum's Acids," *Tetrahedron Letters*, Vol. 48, No. 40, 2007, pp. 7072-7074. http://dx.doi.org/10.1016/j.tetlet.2007.08.012

[18] B. Janardhan, G. Rajitha, V. Ravibabu, B. Rajitha and A. C. Peter, "An Eco-Friendly Improved Protocol for the Synthesis of Bis(3-indolyl)methanes Using Poly(4-vinylpyridinium)hydrogen Sulfate as Efficient, Heterogeneous, and Recyclable Solid Acid Catalyst," *ISRN Organic Chemistry*, Vol. 2013, 2013, pp. 1-5.

[19] Z. H. Jun, J. T. Li and Y. J. Bian, "Pinacolization of Aromatic Aldehydes Using Zn/Montmorillonite K10-$ZnCl_2$ in Aqueous THF under Ultrasound," *Chemical Journal on Internet*, Vol. 5, No. 1, 2003, pp. 8-9.

[20] J. T. Li, X. H. Zhang and Z. P. Lin, "An Improved Synthesis of 1,3,5-Triaryl-2-pyrazolines in Acetic Acid Aqueous Solution under Ultrasound Irradiation," *Beilstein Journal of Organic Chemistry*, Vol. 13, No. 3, 2007, pp. 1-4.

[21] T. P. Caulier and J. Reisse, "On Sonochemical Effects on the Diels-Alder Reaction," *Journal of Organic Chemistry*, Vol. 60, No. 7, 1996, pp. 2547-2548. http://dx.doi.org/10.1021/jo9520203

[22] M. M. Mojtahedi, M. S. Abaee, M. Samianifard, A. Shamloo, M. Padyab, A. W. Mesbah and K. Harms, "Ultrasound Mediation for Efficient Synthesis of Monoarylidene Derivatives of Homo- and Heterocyclic Ketones," *Ultrasonics Sonochemistry*, Vol. 20, No. 3, 2013, pp. 924-930. http://dx.doi.org/10.1016/j.ultsonch.2012.11.004

[23] A. Lahyani, M. Chtourou, M. H. Frikha and M. Trabels, "Amberlyst-15 and Amberlite-200C: Efficient Catalysts for Aldol and Cross-Aldol Condensation under Ultrasound Irradiation," *Ultrasonics Sonochemistry*, Vol. 20, No. 5, 2013, pp. 1296-1303. http://dx.doi.org/10.1016/j.ultsonch.2013.01.017

[24] N. Yan, B. Xiong, W. L. Liao and Z. H. Xu, "Catalytic Synthesis of 1,3-Dioxane-4,6-dione by $La(OTf)_3$," *Chinese Journal of Organic Chemistry*, Vol. 30, No. 30, 2010, pp. 1391-1394.

[25] Z. H. Xu, C. H. Lin and J. H. Xia, "An Efficient Synthesis of 1,3-Dioxane-4,6-diones by Boric Acid," *Heterocyclic Letters*, Vol. 3, No. 3, 2013, pp. 319-323.

[26] F. P. Xu, W. F. Ding and B. L. Da, "Reactions of 2,2-Pentamethylene-1,3-dioxan-4,6-dione with Triethyl Orthoformate and Aromatic Amines," *Chinese Journal of Organic Chemistry*, Vol. 11, No. 3, 1991, pp. 318-321.