

Metal Free Friedel-Crafts Di-acetylation of Resorcinol in Acetic Acid

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Received: 1 August 2016;

Accepted: 15 December 2016;

Published online: 31 January 2017;

AJC-18237

Conventionally, the metal catalyst used for Friedel-Crafts acetylation is poisonous and the acetylating agent is not readily available. Herein, methane sulfonic acid is developed to perform Friedel-Crafts diacetylation of aromatics instead of metal catalyst. Furthermore, acetic acid is employed as acetylating agent to replace acetic anhydride. By this approach, 4,6-diacetylresorcinol, known as an indispensable intermediate in superior fiber polybenzoxazole synthesis, is prepared in high yield from resorcinol. The results obtained by ¹H NMR, FT-IR and HPLC analysis indicate that methane sulfonic acid is an efficient catalyst for Friedel-Crafts acetylation and acetic anhydride can be avoided by replacement with acetic acid, in which phosphorus pentoxide is helpful to improve conversion of desired product.

Keywords: Acetic acid, Acetic anhydride, Acetylation, 4,6-Diacetylresorcinol, Friedel-Crafts reaction, Methane sulfonic acid.

INTRODUCTION

Friedel-Crafts (FC) acylation is usually utilized to synthesize aromatic ketones, which are widely used in the pharmaceutical, fine chemical and other reactive intermediates [1,2]. Hence, a number of attempts have been devoted to improve the catalyst and acylating agent during Friedel-Crafts acylation. Conventionally, electrophilic acylation is mostly catalyzed by Lewis acids (such as ZnCl₂, AlCl₃, FeCl₃, SnCl₄, TiCl₄, ZrCl₄ and BF₃) or Brønsted acids (such as HF, PPA and H₂SO₄) [3-9]. In particular, the use of metal halides causes problems associated with the strong complex formed between ketone product and metal halide itself, which provokes the use of more than stoichiometric amounts of catalyst [1]. In other words, catalyst in acylation is in great demand, which increases cost of desired product preparation. Besides, it is poisonous to the environment, leading to waste disposal problems and it also complicates reaction operation by increasing viscosity of reaction solution.

Therefore, a simple, green and efficient method is in demand to prepare acylated aromatics. As a result, some studies on environment acceptable catalysts development are underway to improve the acylation [1,2,10,11]. For example, 2,4-dihydroxyacetophenone was synthesized from resorcinol in the presence of a variety of solid acid catalysts [1,2]. Moreover, acetylation of activated aromatics was investigated without any added acid catalyst and 2,4-dihydroxyacetophenone has

also been synthesized in such a green way [11]. However, 2,4-dihydroxyacetophenone cannot be further di-acetylated, resulting in main production as mono-acetylated aromatic compound.

Besides, methane sulfonic acid (MSA), recognized as a strong, stable and biodegradable Brønsted acid, is usually used as catalyst and solvent for some condensation or rearrangement reactions [12-17]. Generally, methane sulfonic acid based catalyzed systems containing P₂O₅ or Al₂O₃, are proven to be efficient for acylation of activated aromatics [13,14]. Fries rearrangement of phenolic esters was performed to synthesize acylaryl methane sulfonates catalyzed by POCl₃ with methane sulfonic acid. Furthermore, Fries rearrangement of anilides was carried out in the presence of mixture of P₂O₅ and methane sulfonic acid, which was reported to be an efficient reagent for selective synthesis of *p*-aminoaryl ketones [15]. Moreover, mixture of alumina in methane sulfonic acid is used to prepare *o*-hydroxy-arylketones by acylation of phenol and naphthol derivatives with carboxylic acids or Fries rearrangement of phenolic esters. However, to the best of our knowledge, the individual methane sulfonic acid has not been employed as catalyst in Friedel-Crafts acylation. Thus, as a biodegradable and easy-to-handle liquid, methane sulfonic acid is expected to work in acylation of activated aromatics.

In addition, acetyl chloride, acetic anhydride and acetic acid are known as acetylating agent [18,19]. Acetylation activity of acetyl chloride is high, whereas it is poisonous,

giving bad smell and generating byproduct as hydrochloric acid [2]. Owing to its high reactivity and good controllability, acetic anhydride is in favour over acetyl chloride. However, acetic anhydride is a restricted chemical due to its potential use in narcotics, therefore, it is not readily available even for laboratory purposes. It also gives acetic acid as byproduct, resulting in poor atom economy. Besides, the anhydrides are always commercially produced from the corresponding acids by dehydration. In the current drive toward less wasteful and more environmentally friendly processes, where the emphasis is on atom efficiency and recyclability, a number of attempts have been devoted to the acetylation of resorcinol by employing acetic acid as acetylating agent [18]. However, acetic acid has low acetylating activity, which is usually not effective in di-acetylation of aromatic compounds. In other words, 4,6-diacetylresorcinol can't be efficiently synthe-sized with acetic acid. Thus, it is meaningful to achieve di-acetylation of resorcinol in acetic acid.

As known, 4,6-diacetylresorcinol, which is commercially important intermediate for preparation of 4,6-diamino-resorcinol dihydrochloride (DAR·2HCl) and further superior aromatic polybenzoxazole, is usually prepared by Friedel-Crafts di-acetylation of resorcinol [20-22]. However, the conventional di-acetylation of resorcinol was performed with acetic anhydride and 2 molar excess of metal containing catalyst as zinc chloride is required, which also caused waste disposal problems. Hence, the aim of this work is to develop greener way for di-acetylation of resorcinol. This paper dealt with di-acetylation of resorcinol by employing methane sulfonic acid as catalyst and acetic acid as acetylating agent. Hopefully, 4,6-diacetylresorcinol can be successfully synthesized in high yield in the presence of methane sulfonic acid and acetic acid. Furthermore, the catalyst may be recycled and reused, which is in consonance with the principles of green chemistry.

EXPERIMENTAL

Resorcinol (99.5 %), ZnCl_2 (≥ 98.0 %), acetic anhydride (≥ 98.5 %), acetic acid (≥ 99.5 %), P_2O_5 (≥ 98.0 %), methane sulfonic acid (≥ 99 %) and methanol (≥ 99.5 %) were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received. The water used was purified by filtration through Millipore Gradient system after distillation, giving a resistivity not more than $18.2 \text{ M}\Omega \text{ cm}$.

All proton nuclear magnetic resonance (^1H NMR) spectra were determined on a Bruker DMX-400 instrument with $\text{DMSO-}d_6$ as solvent and TMS as internal standard. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker VECTOR-22 IR spectrometer. The reaction was tracked by HPLC on the Ultimate 3000 HPLC instrument using water and acetonitrile containing 5 mmol L^{-1} trifluoroacetic acid as eluent.

Friedel-Crafts di-acetylation of resorcinol in acetic anhydride: Resorcinol (5.5 g, 0.05 mol), acetic anhydride, were added into a 100 mL three-neck round-bottomed flask with a mechanical stirrer. After resorcinol dissolved in the acetic anhydride, methane sulfonic acid was added. Then the oil bath was raised to a predetermined temperature and the reaction was allowed to proceed for several hours. Samples were collected for HPLC analysis every 30 min. The mixture was

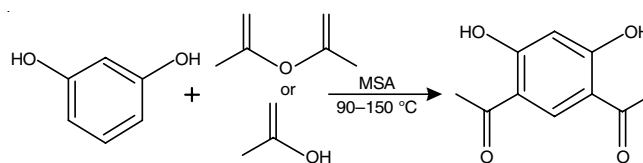
then cooled to room temperature and poured into cool mixture of water and methanol. Afterwards, the product was collected by vacuum filtration and dried under vacuum at 40°C .

Friedel-Crafts di-acetylation of resorcinol in acetic acid: Resorcinol, P_2O_5 and acetic acid were added into a three-neck round-bottomed flask with mechanical stirrer. The mixture was stirred and methane sulfonic acid was added. Afterwards, the reaction was allowed to proceed for several hours in a predetermined temperature, where samples were collected for HPLC analysis every 30 min. The mixture was then cooled and poured into water and methanol mixture. Finally, the product was collected by vacuum filtration and vacuum dry.

Into a 1000 mL glass flask, equipped with a mechanical stirrer and a nitrogen inlet/outlet, were placed 400 mL water. 4,6-diaminoresorcinol dihydrochloride (4.26 g, 0.02 mol) was added. One equimolar amount of 2,6-pyridinedicarboxylic acid (PDA, 0.02 mol) dissolved in NaOH (0.04 mol) aqueous solution was slowly added. Afterwards, the mixture was heated to 90°C for 10 min and DAR-PDA salt solid precipitated, then the product was collected in nitrogen atmosphere. The product was dried under vacuum at 60°C for 48 h.

RESULTS AND DISCUSSION

In general, Friedel-Crafts di-acetylation of resorcinol was performed by using metal catalyst as ZnCl_2 and the required molar ratio of the acid catalyst to resorcinol is at least 2:1, which causes high pollution to environment. Thus, it is meaningful to develop a novel and green catalyst to achieve the di-acetylation. As known, methane sulfonic acid is usually used as catalyst and solvent in some condensation or rearrangement reactions [12-17], besides, it processes readily biodegradable and environmentally acceptable feature, methane sulfonic acid is therefore preferred in this system. As expected, by catalyzed by methane sulfonic acid, 4,6-diacetylresorcinol was successfully synthesized in high yield shown in **Scheme-I**, which was confirmed by ^1H NMR, FT-IR and HPLC analysis.



Scheme-I: Friedel-Crafts di-acetylation of resorcinol in the presence of methane sulfonic acid

As shown in Fig. 1, the peak a at 6.4 ppm is ascribed to the proton (1H) of aromatic ring adjacent to OH group and the peak b at 8.2 ppm is ascribed to the proton (1H) of aromatic ring adjacent to the acyl group and the peak c at 12.9 ppm is ascribed to protons (2H) of OH and the peak d at 2.6 ppm is ascribed to methane protons (6H) of acetyl group. The integration ratio of a:b:c:d is 1:1:2:6, which is consistent with the structure of 4,6-diacetylresorcinol.

As FTIR spectra of obtained 4,6-diacetylresorcinol shown in Fig. 2, band assignments around at about 1622 cm^{-1} is attributed to the $\text{C}=\text{O}$ stretching vibrations of aromatic ketone, band at about 1578 cm^{-1} and 1483 is corresponding to C-C stretching vibrations of aromatic rings.

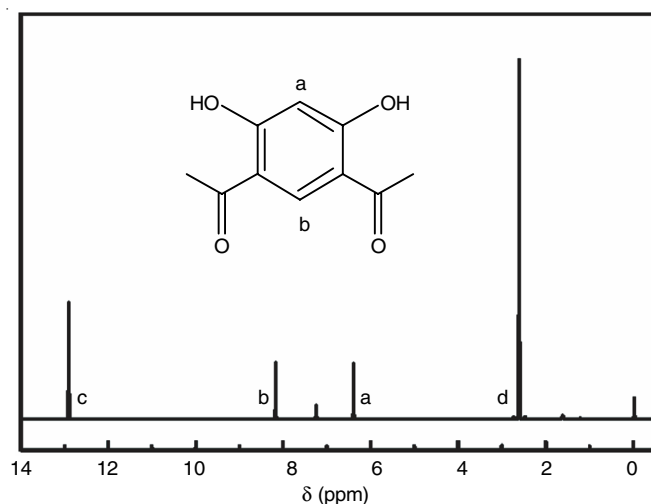


Fig. 1. ^1H NMR spectra of the 4,6-diacetylresorcinol prepared by Friedel-Crafts di-acetylation of resorcinol

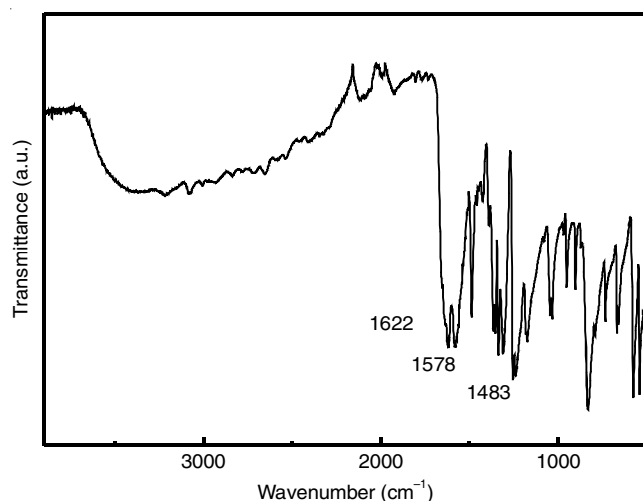


Fig. 2. FTIR spectra of obtained 4,6-diacetylresorcinol prepared by Friedel-Crafts di-acetylation of resorcinol

HPLC results of the product (Fig. 3) shows the same retention time as authentic 4,6-diacetylresorcinol sample, which indicates that the product is the di-acetylated product.

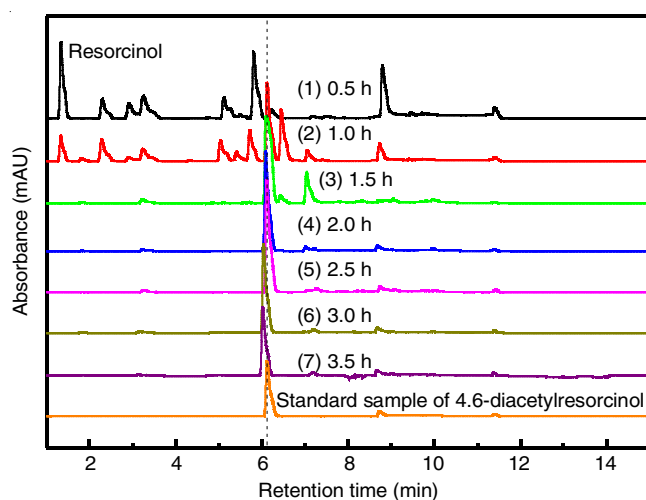


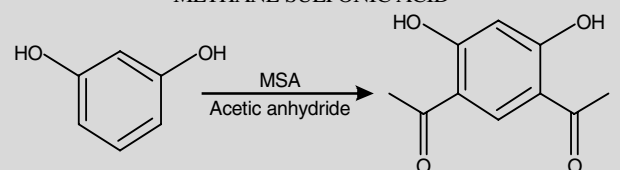
Fig. 3. HPLC spectra of the generated 4,6-diacetylresorcinol as a function of time during Friedel-Crafts di-acetylation of resorcinol, which was performed in acetic anhydride catalyzed by methane sulfonic acid

Moreover, as the reaction time increases, the content of resorcinol decreases and the desired product increases. It further confirmed that 4,6-diacetylresorcinol was successfully synthesized. The results also imply that methane sulfonic acid is an efficient catalyst for the resorcinol di-acetylation. It implies that methane sulfonic acid is a feasible catalyst for Friedel-Crafts di-acetylation.

A series of experiments were carried out to investigate influence on Friedel-Crafts acetylation by using methane sulfonic acid as catalyst. The results (1-1 to 1-10) are summarized in Table-1. There is no doubt that temperature plays a great role in the reaction. As list in Table-1 and shown in Fig. 4a, different temperature from 90 to 150 °C were performed to optimize the temperature for the reaction. Experiment 1-1, 1-2, 1-3 and 1-4 were respectively carried out at 90, 110, 130, 150 °C, with molar ratio of methane sulfonic acid/acetic anhydride/resorcinol 2:2:1. For experiment 1-1 performed at 90 °C, the conversion of di-acetylated resorcinol gradually increases with increase of reaction time; it reaches 79 % after 4 h. In the case of reaction at 110 °C (1-2), the conversion increases to 84.6 % in 1.5 h and then slightly decreases to 82.2 % in 4.0 h. For reaction at 130 °C (1-3), the conversion increases to 90.5 % in 1.0 h and then slightly decreases to 84.1 % after 4.0 h. And for reaction at 150 °C (1-4), the conversion increases to 89.6 % in 0.5 h and then drops to 39 % after 4.0 h. Clearly, conversion of the desired product increases to a maximum value and then decreases, which is probably due to decomposition of desired product at high temperature. Moreover, higher temperature results in higher reaction rate. Hence, it can be found that 110-130 °C is a suitable temperature range for the reaction, since conversion can reach to high value in short time and there is only slight product decomposition. Therefore, all further experiments were carried out at 130 °C.

It is known that Friedel-Crafts acetylation of resorcinol is influenced not only by reaction temperature, but also the

TABLE-1
FRIEDEL-CRAFTS DI-ACETYLATION OF RESORCINOL
WITH ACETIC ANHYDRIDE CATALYZED BY
METHANE SULFONIC ACID



Entry	Temp. (°C)	Molar ratio ^a	Time (h) ^b	Conversion (%) ^c
1-1	90	2:2:1	4.0	79.0
1-2	110	2:2:1	1.5	84.6
1-3	130	2:2:1	1.0	90.5
1-4	150	2:2:1	0.5	89.6
1-5	130	1:2:1	2.5	86.1
1-6	130	(0.5):2:1	7.0	76.8
1-7	130	(0.1):2:1	—	—
1-8	130	2:1:1	0.5	62.0
1-9	130	2:2:1*	0.5	8.6
1-10	130	2:5:1*	1.0	17.8

^aMolar ratio of methane sulfonic acid/acetic anhydride/resorcinol,

*Acetic acid is used as acetylating agent instead of acetic anhydride;

^bTime to reach the highest conversion of 4,6-diacetylresorcinol from resorcinol; ^cConversion of 4,6-diacetylresorcinol from resorcinol, --no desired product was obtained.

catalyst dosage. Therefore, the amount of methane sulfonic acid was screened and the results are listed in Table-1 and Fig. 4b, molar ratio of methane sulfonic acid to resorcinol varies from 2:1 to 0.1:1. Experiment 1-3, 1-5, 1-6 and 1-7 are respectively corresponding to the reaction performed with molar ratio of methane sulfonic acid/resorcinol 2:1, 1.0:1, 0.5:1 and 0.1:1, with molar ratio of acetic anhydride/resorcinol 2:1 at 130 °C. For experiment 1-5 operated with molar ratio of methane sulfonic acid/resorcinol only 1.0:1, the conversion can reach 86.1 % after 2.5 h. And for 0.5:1, the conversion reaches 76.8 % after 7 h (data not shown). However, when the ratio is 0.1:1, no di-acetylated resorcinol can be observed. It indicates that methane sulfonic acid is indispensable in the reaction but small amount of catalyst used can also result in high yield of 4,6-diacetylresorcinol preparation. Note that more than 2:1 of molar ratio of catalyst/resorcinol was required in conventional method.

Furthermore, as shown in Fig. 4c, influence of the molar ratio of acetylating agent/reactant on Friedel-Crafts di-acetylation of resorcinol was also examined. Compared with reaction performed with acetic anhydride/resorcinol molar ratio 2:1, the conversion obtained with ratio of acetic anhydride/resorcinol 1:1 is much lower, which can only reach 62.0 %. Hence, acetylating agent dosage plays a critical role in the

di-acetylation of resorcinol. It also indicates that more than 2:1 of acetylating agent/reactant is required to achieve the di-acetylation and the generated acetic acid is unable to further acetylate the mono-acetylated resorcinol into di-acetylated product. In other words, atom economy is poor by using acetic anhydride as acetylating agent.

Besides, acetic anhydride is usually made from acetic acid and it also gives acetic acid as byproduct after acetylation. In addition, it is strictly controlled because it is a precursor chemical of narcotics, thus, acetylating agent is not readily available even for laboratory purposes. Based on the disadvantages of these most frequently used acetylating agents, it is expected to be replaced by low-cost and benign agents. In this connection, acetic acid is a better choice. Therefore, it would be meaningful if the acetylation could be achieved using acetic acid as acetylating agent. As the experiment 1-9 and 1-10 shown in Table-1 and Fig. 4d, Friedel-Crafts di-acetylation is carried out in acetic acid. Clearly, the conversion of di-acetylated resorcinol is low, only 8.6 % while performed with 2:1 ratio of acetic acid/resorcinol at 130 °C. It is understandable that the generated water induces hydrolysis of reaction intermediate and lowers the yield [12]. Although the conversion of 4,6-diacetylresorcinol using acetic acid as acetylating agent increases when more acetic acid is used (8.6 % in experiment

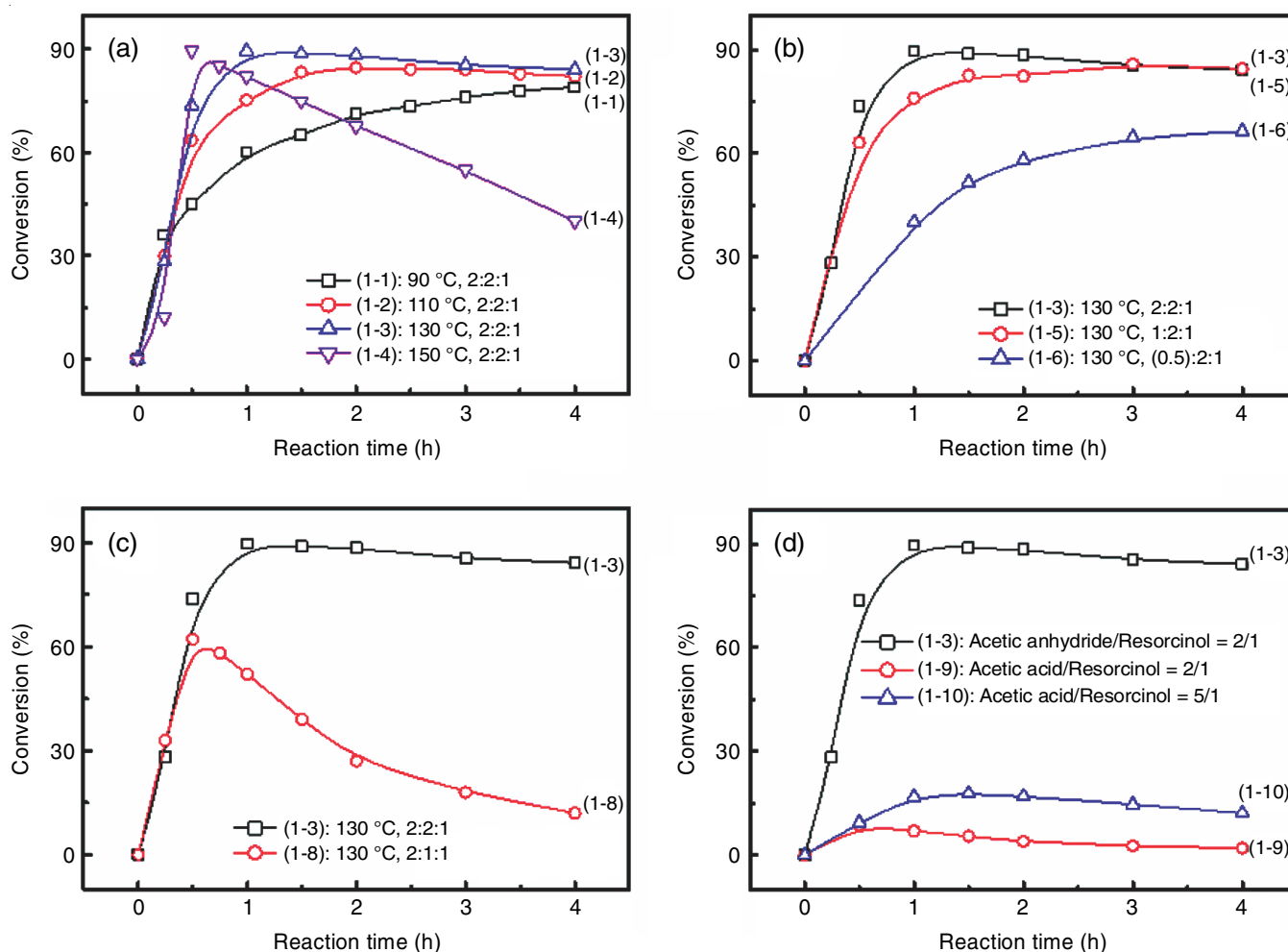


Fig. 4. Conversion of 4,6-diacetylresorcinol as a function of reaction temperature (a), methane sulfonic acid dosage (b), acetic anhydride dosage (c) and acetylating agent (d) by Friedel-Crafts di-acetylation of resorcinol performed in acetic anhydride

1-9 vs. 17.8 % in experiment 1-10), the acetylation of resorcinol in acetic acid is still too low for practical use. Therefore, di-acetylation of resorcinol with acetic acid is expected to be achieved in high conversion.

By assuming that generated water prevents the further acetylation of resorcinol, P_2O_5 was introduced into methane sulfonic acid based catalytic system to improve the di-acetylation of resorcinol with acetic acid in high yield. More specifically, the generated water can be absorbed by P_2O_5 during the di-acetylation process, which facilitates the reaction [11]. As expected, P_2O_5 significantly help to improve the yield of desired product. Similarly, effect of temperature, acetylating agent and catalyst dosage on Friedel-Crafts di-acetylation of resorcinol is examined. As shown in Fig. 5a, different temperatures varied from 90-130 °C were studied to consider the proper temperature for the reaction with molar ratio of P_2O_5 /methane sulfonic acid/acetic acid/resorcinol 0.70:2:5:1. Consequently, as time increases, the conversion of the desired product increases to a maximum value and then decreases. For experiment 2-1, 2-2 and 2-3 were respectively performed at 90, 110, 130 °C, they reaches 74.2 % after 5.0 h, 89.0 % in 1.5 h and 90.6 % in 1.0 h (Table-2). That is, the reaction at 130 °C exhibits a highest conversion. Therefore, 110-130 °C is suitable for the reaction, whose conversion of the desired product can reach a high value

in short time. Fig. 5b shows the results of di-acetylation of resorcinol performed with different molar ratio of acetic acid/resorcinol. The molar ratio of acetic acid to resorcinol was varied from 5:1 to 2:1. For comparison with experiment 2-3 with molar ratio of P_2O_5 /methane sulfonic acid/acetic acid/resorcinol 0.70:2:5:1, the experiment 2-4 operated with molar ratio of P_2O_5 /MSA/acetic acid/resorcinol 0.70:2:3:1 has the conversion of 87.8 % in 1.0 h (Table-2). Similarly, for experiment 2-5 with 2:1 of acetylating agent/resorcinol used, the conversion can reaches 83.5 % (Table-2). It is clearly that less acetic acid can also achieve high di-acetylation conversion, which could improve atom economy of the di-acetylation. In order to keep the conversion in a constant high value for further studies, the subsequent experiments were performed with molar ratio of acetic acid/resorcinol 5:1.

Furthermore, effect of the catalyst dosage on 4,6-diacetylresorcinol preparation was presented in Fig. 5c. Compared with experiment 2-3 performed with the molar ratio of methane sulfonic acid/resorcinol 2:1, conversion of experiment 2-8 carried out with molar ratio of methane sulfonic acid/resorcinol only 1:1 can reach to 87.1 % after 4.0 h reaction, which indicates that the di-acetylation of resorcinol can be efficiently achieved in high conversion with small amount of methane sulfonic acid used, but longer reaction time is needed. By contrast, for

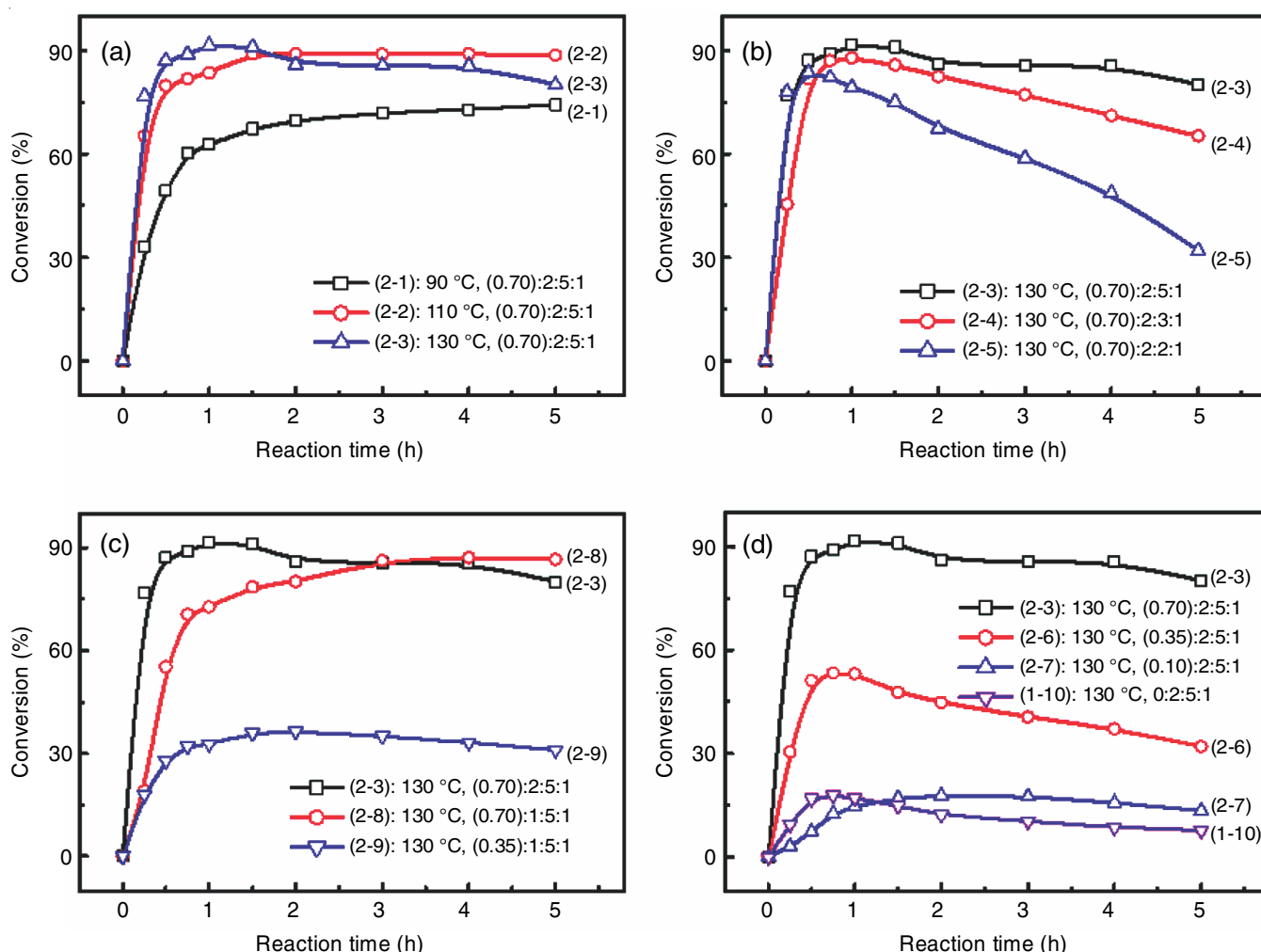


Fig. 5. Conversion of 4,6-diacetylresorcinol as a function of reaction temperature (a), methane sulfonic acid dosage (b), acetic acid dosage (c) and P_2O_5 dosage (d) by Friedel-Crafts di-acetylation of resorcinol performed in acetic acid

TABLE-2
DI-ACETYLATION OF RESORCINOL IN ACETIC
ACID WITH P₂O₅/METHANE SULFONIC ACID

Entry	Temp. (°C)	Molar ratio ^a	Time (h) ^b	Conversion (%)
2-1	90	(0.70):2.5:1	5.0	74.2
2-2	110	(0.70):2.5:1	1.5	89.0
2-3	130	(0.70):2.5:1	1.0	90.6
2-4	130	(0.70):2.3:1	1.0	87.8
2-5	130	(0.70):2.2:1	0.5	83.5
2-6	130	(0.35):2.5:1	1.0	50.8
2-7	130	(0.10):2.5:1	2.0	17.7
2-8	130	(0.70):1.5:1	4.0	87.1
2-9	130	(0.35):1.5:1	2.0	36.4

^aMolar ratio of P₂O₅/methane sulfonic acid/CH₃COOH/resorcinol.
^bTime to reach the highest conversion during the reaction.

experiment 2-9 performed with resorcinol/acetic acid/methane sulfonic acid/P₂O₅ molar ratio 1:5:1:0.35, the conversion is only 36.4 %, which is much lower than that of experiment 2-3 with the same molar ratio of methane sulfonic acid/P₂O₅. This indicates that the P₂O₅ dosage effect a lot in the reaction.

As known, the generated water will prevent the reaction and reduce the conversion of Friedel-Crafts di-acetylation [18]. Therefore, P₂O₅ were introduced to get rid of water in this system, which avoids the degradation of reaction intermediate and promote the desired product formation. Since P₂O₅ dosage in the reaction has remarkable effects on the di-acetylation, the experiments were performed with different amount of P₂O₅ to further understand its corresponding influence. As shown in Fig. 5d, experiment 1-10, 2-3, 2-6 and 2-7 are respectively corresponding to the reaction operated with molar ratio of P₂O₅/resorcinol 0:1, 0.70:1, 0.35:1, 0.10:1. Obviously, when the ratio of P₂O₅/resorcinol is 0.70:1, the corresponding conversion can reaches 90.6 %; but when the ratio of P₂O₅/resorcinol is 0.10:1, the conversion is only 17.7 %. It is understandable that 0.70 equivalent of P₂O₅ can completely get rid of the generated water and 0.35 or 0.10 equivalent of P₂O₅ used leads to some water left and residual water prevent the reaction. In other words, insufficient P₂O₅ used results in lower conversion of desired product. Thus, it is optimized to carry out the experiment with P₂O₅/resorcinol molar ratio more than 0.67:1. On the other hand, the results further demonstrate that P₂O₅ contributes to absorption of generated water.

Conclusion

In conclusion, methane sulfonic acid was employed as catalyst for Friedel-Crafts acetylation, which provides an environmentally acceptable way for acetylation of aromatic compounds. Moreover, resorcinol is successfully di-acetylated by acetic acid instead of acetic anhydride and P₂O₅ is helpful to improve the conversion. And the di-acetylation with acetic anhydride or acetic acid processed high region-selectivity. By this method, 4,6-diacetylresorcinol, a monomer precursor of high performance fiber PBO, was synthesized in high yield,

which also significantly reduces the operation difficulty. More specifically, it can be found that the optimized temperature is 110-130 °C, small amount of methane sulfonic acid usage can also result in high yield of desired product; P₂O₅ dosage plays a great role in the acetylation with acetic acid. Based on the improved atom efficiency and the use of environmental benign catalyst, it is in consonance with the practice of green chemistry.

ACKNOWLEDGEMENTS

Financial support from National Natural Science Foundation of China (51303206) was gratefully acknowledged. The youth innovation fund projects of Chongqing Institute of Green and Intelligent Technology (Y23H040M10) is also acknowledged.

REFERENCES

- G. Sartori and R. Maggi, *Chem. Rev.*, **106**, 1077 (2006); <https://doi.org/10.1021/cr040695c>.
- J. Kaur, K. Griffin, B. Harrison and I.V. Kozhevnikov, *J. Catal.*, **208**, 448 (2002); <https://doi.org/10.1006/jcat.2002.3592>.
- P. Krishnamoorthy, P. Sathyadevi, K. Deepa and N. Dharmaraj, *Spectrochim. Acta A*, **77**, 258 (2010); <https://doi.org/10.1016/j.saa.2010.05.019>.
- E.I. Negishi, V. Bagheri, S. Chatterjee, F.T. Luo, J.A. Miller and A.T. Stoll, *Tetrahedron Lett.*, **24**, 5181 (1983); [https://doi.org/10.1016/S0040-4039\(00\)88391-4](https://doi.org/10.1016/S0040-4039(00)88391-4).
- A. Corma and H. Garcia, *Chem. Rev.*, **103**, 4307 (2003); <https://doi.org/10.1021/cr030680z>.
- G.K.S. Prakash, C. Panja, T. Mathew and G.A. Olah, *Catal. Lett.*, **114**, 24 (2007); <https://doi.org/10.1007/s10562-007-9033-9>.
- G.V.M. Sharma, A.K. Mahalingam, M. Nagarajan, A. Ilangoan and P. Radhakrishna, *Synlett*, 1200 (1999); <https://doi.org/10.1055/s-1999-2806>.
- P. Saravanan and V.K. Singh, *Tetrahedron Lett.*, **40**, 2611 (1999); [https://doi.org/10.1016/S0040-4039\(99\)00229-4](https://doi.org/10.1016/S0040-4039(99)00229-4).
- T.P. Smyth and B.W. Corby, *J. Org. Chem.*, **63**, 8946 (1998); <https://doi.org/10.1021/jo981264v>.
- C.L. Padro and C.R. Apesteguia, *Catal. Today*, **107-108**, 258 (2005); <https://doi.org/10.1016/j.cattod.2005.07.078>.
- J.S. Brown, R. Glaser, C.L. Liotta and C.A. Eckert, *Chem. Commun.*, 1295 (2000); <https://doi.org/10.1039/b001544j>.
- A. Commarieu, W. Hoelderich, J.A. Laffitte and M.P. Dupont, *J. Mol. Catal. Chem.*, **182-183**, 137 (2002); [https://doi.org/10.1016/S1381-1169\(01\)00506-4](https://doi.org/10.1016/S1381-1169(01)00506-4).
- H. Sharghi and B. Kaboudin, *J. Chem. Res.*, 628 (1998); <https://doi.org/10.1039/a800158h>.
- B. Kaboudin, *Phosphorus Sulfur Silicon Rel. Elem.*, **178**, 887 (2003); <https://doi.org/10.1080/10426500307808>.
- B. Kaboudin and Y. Abedi, *Org. Prep. Proced. Int.*, **41**, 229 (2009); <https://doi.org/10.1080/00304940902956093>.
- I. Jeon and I.K. Mangion, *Synlett*, **23**, 1927 (2012); <https://doi.org/10.1055/s-0032-1316568>.
- A.K. Bhattacharya and K.C. Rana, *Mendeleev Commun.*, **17**, 247 (2007); <https://doi.org/10.1016/j.mencom.2007.06.023>.
- G. Yadav and A. Joshi, *Clean Technol. Environ. Policy*, **4**, 157 (2002); <https://doi.org/10.1007/s10098-002-0148-9>.
- T.P. Smyth and B.W. Corby, *J. Org. Chem.*, **63**, 8946 (1998); <https://doi.org/10.1021/jo981264v>.
- J. Kawachi, H. Matsubara and Y. Nakahara and Y. Watanabe, *Process for Producing 4,6-Diaminoresorcinols*, U.S. Patent 5892118 (1999).
- J.F. Wolfe and F.E. Arnold, *Macromolecules*, **14**, 909 (1981); <https://doi.org/10.1021/ma50005a004>.
- E.W. Choe and S.N. Kim, *Macromolecules*, **14**, 920 (1981); <https://doi.org/10.1021/ma50005a006>.