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Ultrasound Promoted Synthesis of α,α'-bis(Substituted Furfurylidene) Cycloalkanones and Chalcones

Ji-Tai Li [a] , Guo-Feng Chen [a] , Jian-Xin Wang [a] & Tong-Shuang Li [a]
[a] Department of Chemistry , Hebei University , Baoding, 071002, P. R. China

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ULTRASOUND PROMOTED SYNTHESIS OF α,α'-BIS(SUBSTITUTED FURFURYLIDENE) CYCLOALKANONES AND CHALCONES

Ji-Tai Li,* Guo-Feng Chen, Jian-Xin Wang and Tong-Shuang Li*

Department of Chemistry, Hebei University, Baoding 071002, P. R. China

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Abstract: Condensation of furfural with cycloalkanones and substituted acetophenones catalysed by potassium hydroxide results α,α'-bis(substituted furfurylidene) cycloalkanones and chalcones in high yield under ultrasound irradiation in 4-50 min.

The chalcones are very common in natural product chemistry.[1] Some chalcones are used as sweeteners, drugs,[2,3] sunscreen agents,[4] photoresits and photographic emulsions[5] or synthesised to test their pharmacological activity.[6,7] The α,α'-bis(substituted furfurylidene) cycloalkanones are used as intermediates of agrochemicals, pharmaceuticals and perfumes.[8] Claisen-Schmidt condensation of furfural with cycloalkanones or acetophenones has been reported in the

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* To whom correspondence should be addressed, e-mail: orgsyn@nic.hbu.edu.cn

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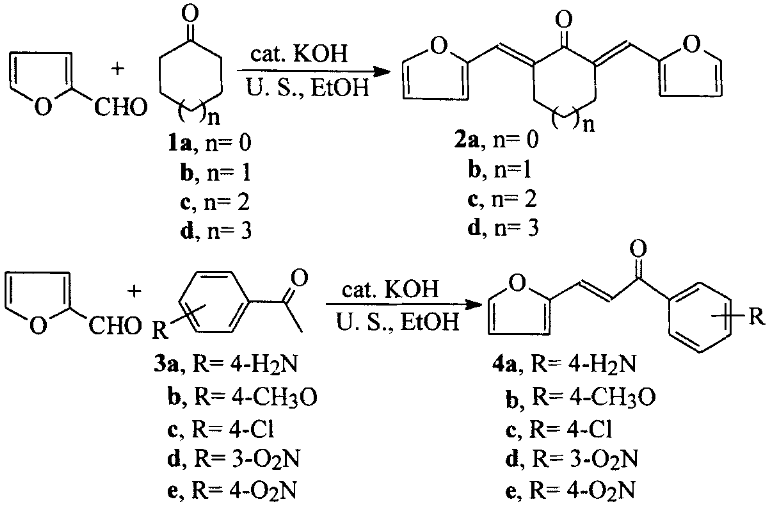
literature.[9-13] However, there were always some troubles due to critic conditions, long reaction time, low yield and difficult work up.

A survey of literature shows that many organic reactions have recently been accelerated by ultrasonic irradiation.[14,15] Since that reaction time gets reduced and yields get improved under ultrasound irradiation condition, we decide to study the possibility of the preparation of α,α'-bis(substituted furfurylidene) cycloalkanones and chalcones using Claisen-Schmidt condensation of furfural with cycloalkanones and acetophenones under ultrasonication. Herein we report a facile synthesis of α,α'-bis(substituted furfurylidene) cycloalkanones and chalcones accelerated by ultrasonic irradiation.

As shown in **Table** and **Scheme**, the synthesis of α,α'-bis(substituted furfurylidene) cycloalkanones (**2a-d**) were carried out in good to excellent yield for Claisen-Schmidt condensation of furfural with cycloalkanones (**1a-d**)



1a, n= 0
b, n= 1
c, n= 2
d, n= 3

2a, n= 0
b, n=1
c, n= 2
d, n= 3

3a, R= 4-H_2N
b, R= 4-CH_3O
c, R= 4-Cl
d, R= 3-O_2N
e, R= 4-O_2N

4a, R= 4-H_2N
b, R= 4-CH_3O
c, R= 4-Cl
d, R= 3-O_2N
e, R= 4-O_2N

Scheme

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Table. Preparation of α,α'-bis(substituted furfurylidene) cycloalkanones and chalcones catalysed by solid potassium hydroxide under ultrasound

Entry	Mole ratio[a]	Time(min)/ Temperature(°C)	Product (Yield %)[b]	m.p. (°C) (Reported)
1a	2:1	30/40	**2a** (85)	164-165(164-165[16])
1b	2:1	40/40	**2b** (94)	143-144(143-144[16])
	1:1.1	20/50	**2b** (91)	143-144
1c	2:1	40/40	**2c** (68)	111-112.5(111-112[16])
1d	2:1	50/40	**2d** (96)	Viscous liquid (Viscous liquid[16])
3a	1:1	10/20	**4a** (96)	111.5-113(114[12])
3b	1:1	12/20	**4b** (90)	77-78(78-79[16])
3c	1:1	5/20	**4c** (91)	75.5-76.5(77-78[16])
3d	1:1	12/20	**4d** (78)	99.5-101(100-101[13])
3e	1:1	4/20	**4e** (95)	146.5-148(150[17])

[a] The mole ratio is furfural : ketone. [b] Isolated yield based on furfural.

catalysed by potassium hydroxide under ultrasound irradiation for 30-50 min in anhydrous ethanol at 20-50 °C. Claisen-Schmidt condensation of furfural with substituted acetophenones (**3a-e**) at room temperature results in high to excellent yield of chalcones (**4a-e**) within 4-12 min. Compared with literature reported,[9,11-13,17] the mainly advantages of present procedure are milder conditions, higher yield, shorter reaction period and simple workup.

It is worth noting that the size of cycloalkanones (**1a-d**) and the electronic effect of subsituents in acetophenones (**3a-e**) seem to be no affect to the yield of the products. In anion exchange resin catalyzed manner,[11] an aqueous alcohol solution of furfural and ketone was agitated for several hours at 37 °C to furnish α,α'-bis(furfurylidene) cyclopentanone (**2a**), α,α'-bis(furfurylidene) cyclohexanone (**2b**) and α,α'-bis(furfurylidene) cycloheptanone (**2c**) in 10 %, 15 % and 30 % yield respectively. Whereas our procedure results in 85 %, 94 % and 68 % yield respectively within 40 min (entries **1a-c**). To test the selectivity of the reaction, we carried out the reaction in ratio (furfural/cyclohexanone) of 2 : 1 and 1 : 1.1 (entry **1b**). Both the reaction provided the same product α,α'-bis(furfurylidene) cyclohexanone (**2b**), α-(furfurylidene) cyclohexanone was not obtained.

In conclusion, ultrasound can accelerate the Claisen-Schmidt condensation of furfural with cycloalkanones or acetophenones to furnish α,α'-bis(substituted furfurylidene) cycloalkanones and chalcones in high yield catalysed by potassium hydroxide with easy workup.

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EXPERIMENTAL

Furfural is purified by distillation prior to use. Melting points were uncorrected. IR spectra were recorded on a Bio-Rad FTS-40 spectrometer (KBr). ^{1}H NMR spectra were measured on VXR-300S spectrometer by using TMS as internal standard and $CDCl_3$ as solvent. Mass spectra were determined on a VG-7070E spectrometer (EI, 70 eV). Sonication was performed in a Shanghai Branson-CQX ultrasonic cleaner with a frequency of 25 KHz and a nominal power 500 W. The reaction flask was located at the maximum energy area in the cleaner and the temperature of water bath was controlled by addition or removal of water.

General procedure: To a 50 ml Pyrex flask was charged with furfural (20 mmol), cycloalkanones (**1**, 10 mmol) or acetophenones (**3**, 20 mmol), ethanol (10 ml) and catalytic quantity of potassium hydroxide (3.25 mmol). The mixture was irradiated in the water bath of an ultrasonic cleaner at the temperature for the period as indicated in **Table** (sonication was continued until crystals were appeared or furfural was disappeared indicated by TLC). After cooling in an ice-water bath, the formed product was collected by filtration and washed with water till the washings were neutral. The authenticity of the products was established by their melting points and spectral data.

2d: ν_{max} 3125, 1685, 1600, 1560, 1080, 1020 cm^{-1}; δ_H 1.71-1.80 (6H, m, 4,5,6-H_6), 2.89 (4H, t, J = 6.3 Hz, 3,7-H_4), 6.48 (2H, d, J = 3.3 Hz, 4', 4''-H_2), 6.53 (2H, d, J = 3.3 Hz, 3',3''-H_2), 6.84 (2H, s, vinyl-H_2), 7.49 (2H, s, 5',5''-H_2) ppm; m/z (%): 282 (M^+, 100), 254 (5), 225 (6), 176 (15), 161 (15), 147 (15), 133 (17), 120 (30), 107(32).

4a: ν_{max} 3448, 3442, 3350, 3325, 3250, 1640, 1600, 1580, 1550, 1335, 1280, 1180,1075 cm^{-1}; δ_H 4.19 (2H, brs, NH_2), 6.48 (1H, d, J = 3.3 Hz, fur-4''-H), 6.65 (1H, d, J = 3.3 Hz, fur-3''-H), 6.68 (2H, d, J = 8.4 Hz, Ph-3',5'-H), 7.46 (1H, d, J = 15.0 Hz, 3-H), 7.49 (1H, s, fur-5''-H), 7.56 (1H, d, J = 15.0 Hz, 2-H), 7.92 (2H, d, J = 8.4 Hz, Ph-2',6'-H) ppm; m/z (%): 213 (M^+, 54), 185 (19), 159 (32), 135 (19), 120 (100), 92 (52), 77 (6), 65 (80), 52 (9).

4d: ν_{max} 3150, 3125, 3075, 1680, 1600, 1530, 1345, 1290, 1260, 1220, 1020 cm^{-1}; δ_H 6.56 (1H, d, J = 3.3 Hz, fur-4''-H), 6.81 (1H, d, J = 3.3 Hz, fur-3''-H), 7.45 (1H, d, J = 15.0 Hz, 2-H), 7.59 (1H, s, fur-5''-H), 7.68 (1H, d, J = 15.0 Hz, 3-H), 7.72 (1H, t, J = 7.4 Hz, Ph-5'-H), 8.36 (1H, d, J = 7.5 Hz, Ph-6'-H), 8.43 (1H, d, J = 8.4 Hz, Ph-4'-H), 8.85 (1H, s, Ph-2'-H) ppm; m/z (%): 243 (M^+, 43), 215 (6), 196 (6), 189 (12), 169 (12), 150 (100), 141 (17), 121 (66), 115 (19), 104 (44), 65 (77).

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4e: ν_{max} 3175, 3145, 3125, 1660, 1610, 1590, 1550, 1520, 1325, 1225, 1025 cm^{-1}; δ_H 6.56 (1H, d, J = 3.3 Hz, fur-4″-H), 6.81 (1H, d, J = 3.3 Hz, fur-3″-H), 7.42 (1H, d, J = 15.0 Hz, 2-H), 7.56 (1H, s, fur-5″-H), 7.64 (1H, d, J = 15.0 Hz, 3-H), 8.16 (2H, d, J = 8.7 Hz, Ph-2′,6′-H_2), 8.35 (2H, d, J = 8.7 Hz, Ph-3′,5′-H_2) ppm; m/z (%): 243 (M^+, 60), 227 (3), 215 (4), 196 (11), 189 (13), 168 (10), 150 (100), 141 (12), 121 (62), 115 (17), 104 (26), 92 (13), 76 (24), 65 (54).

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REFERENCES

1. Comdes, G.; Vassort, P. and Winternitz, F. *Tetrahedron Lett.* **1986**, *26*, 5981.
2. Misra, S.S. and Tenari, R.S. *J. Indian Chem. Soc.* **1973**, *50*, 68.
3. Lafon, L. *Ger Offen 2,010,180*, **1970**, (*Chem. Abstr.* **1970**, *73*, 120342).
4. Suetsugu, K and Tomita, S. Jpn. Kohai Tokkyo *JP 62,158,206*, **1987**.
5. Yasui, S.; Noguchi, A. and Yokoyama, Y. Jpn. Kokai Tokkyo Koho *JP 04 36750*, **1992**.
6. Chen, F.C.; Chen, Y.H. and Chen, L.S. *Tai-Wan K'o Hsuch,* **1972**, *26*, 96.
7. Hsu, K.K; Lin, Y.C.; Su, c.T. and Lien, E.J. *Tai-wan Yao Hsueh Tsa Chih.* **1982**, *34*, 71.
8. Ogawa, M.; Ishii, Y.; Nakano, T. and Irifune, S. Jpn. Kohai Tokkyo *JP 63 238034*, **1988**.
9. Alexander, K.; Hafner, L.S.; Smith, G.H. and Schniepp, L.E. *J. Am. Chem. Soc.* **1950**, *72*, 5506.
10. Leonard, N.J.; Miller, L.A. and Berry, J.W. *J. Am. Chem. Soc.* **1957**, *79*, 1482.

11. Austerwell, G.V. and Pallaud, R. *Bull. Soc. Chim. Fr.* **1953**, 678.

12. Kushwaha, D.S.C. and Lal, J.B. *Indian J. Chem.* **1967**, *6*, 82.

13. Turner, D.L. *J. Am. Chem. Soc.* **1949**, *71*, 612.

14. Eshuis, J.J.W. *Tetrahedron Lett.* **1994**, *35*, 7833.

15. Li, J.T.; Li, L.J.; Li, T.S.; Li, H.Z. and Liu, J.K. *Ultrasonics Sonochemistry* **1996**, *3*, S141.

16. Babu, G. and Perumal, P.T. *Synth. Commun.* **1997**, *27*, 3677.

17. Ariyan, Z.S. and Suschitzky, H. *J. Chem. Soc.* **1961**, 2242.

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