SHORT PAPER

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A convenient synthesis of 2-aroyl-3,5-diarylfuran under microwave irradiation[†]

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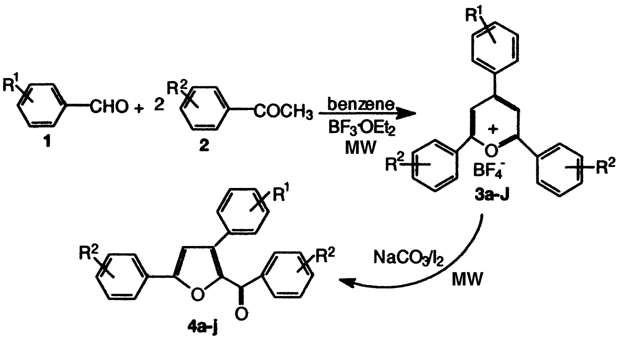
A simple, rapid and efficient method for the synthesis of 2-aroyl-3,5-diarylfuran under microwave irradiation is described. The effect of microwave irradiation power, times and solvent on the reaction is investigated.

Keywords: aldehyde, acetophenone, 2,4,6-triarylpyrylium salts, microwave irradiation

2,4,6-Triarylpyrylium salts are very useful intermediates in synthetic organic chemistry and may be converted in good yields into other functional groups.[1–5] On the basis of literature methods,[6] we have obtained a large number of 2,4,6-triarylpyrylium salts using one equivalent of substituted benzaldehydes **1** with two equivalents of substituted acetophenones **2** mediated by boron trifluoride etherate in benzene under microwave irradiation conditions. Pedersen[7] reported the conversion of the 2,4,6-triphenylpyrylium salt into 2-benzoyl-3,5-diphenylfuran by the action of base in the presence of iodine. The reaction is thought to involve iodination of the anion of the pseudobase followed by intramolecular displacement of iodide ion. However, in general, this reaction suffers from a long reaction time (18 h) and low yield. Thus, the scope of this reaction was not explored. Aroyl-containing furan derivatives are the starting materials for the synthesis of both (+) and (–) enantiomers of frontalin.[8] Also, for the development of anti-pneumocystis carinii agents we needed quantities of 2,4-diarylfuran.[9] Reacting 2-aroyl-3,5-diarylfuran and potassium *tert*-butoxide in dioxane under mild conditions produced dearoylation and is the best way to obtain 2,4-diarylfuran.[10]

In recent years, microwave (MW) irradiation using commercial domestic ovens has been used to accelerate organic reactions, the high heating efficiency giving rise to remarkable rate increments and drastic reduction of reaction times; some important reviews have been published.[11] At the same time, some important reviews about the microwave irradiation synthesis of heterocyclic compounds have been published.[12] Recently, we have also reported palladium[13,14] and copper-catalysed[15,16] cross-coupling reactions under microwave irradiation. The current paper reports a general reaction for a variety of substitutents on the aryl rings proceeding to give reasonable yields of 2-aroyl-3,5-diarylfuran **4a–j** under microwave irradiation conditions. A comparative study on the reaction shows that the method offers the possibility of considerably decreasing the reaction time and improving the yield compared to conventional conditions. This method is simple, rapid and affords good yields. The reactions are shown in Scheme 1 and corresponding results are summarised in Table 1.

We have investigated the effect of the power and time of microwave irradiation on the second stage of Scheme 1, the reaction of 2,4,6-triphenylpyrylium salts with aqueous sodium carbonate and iodine. The optimum results are summarised in Table 1. The results shown that a high yield of compound **4a** can be obtained at 450 W power for 10 min continuous irradiation.



Scheme 1

The efficiency of various solvents on the second stage, formation of 2-aroyl-3,5-diarylfuran, was studied and acetone was found to be the best solvent for the reaction. Other solvents were also studied and their efficiencies are in the order: acetone ≈ trichloromethane > benzene > DMF > ethanol. Specially, when ethanol is used as solvent in this reaction, the yield of compound **4a** is poor. Water also influences the reaction; there is no reaction in the second stage when there is no water present in that stage.

Table 1 The reaction of aryl aldehydes and aryl acetophenone under microwave irradiation[a]

Aldehyde	Acetophenone	Substituents	Product	Yield/%[b]
1a	2a	R^1=H, R^2=4-Br	4a	85
1b	2b	R^1=H, R^2=4-Cl	4b	88
1c	2c	R^1=4-OCH_3, R^2=H	4c	81
1d	2d	R^1=4-OCH_3, R^2=4-CH_3	4d	85
1e	2e	R^1=4-OCH_3, R^2=4-Br	4e	89
1f	2f	R^1=4-OCH_3, R^2=4-Cl	4f	87
1g	2g	R^1=4-Cl, R^2=H	4g	90
1h	2h	R^1=4-Cl, R^2=4-Cl	4h	94
1i	2i	R^1=4-Cl, R^2=4-Br	4i	86
1j	2j	R^1=4-Cl, R^2=4-CH_3	4j	92

[a]Irradiation conditions: (i) power 450W, time 6-8min (for the synthesis of 2,4,6-triarylpyryliums), (ii) power 450W, time 8–10min (for the synthesis of 2-aroyl-3,5-diarylfuran); [b]isolated yields; [c]all new compounds were characterised by ^1H NMR, MS, and microanalyses.

Experimental

^1H NMR Spectra (200 Hz) were recorded in $CDCl_3$ using an FT-80 Spectrometer. Mass Spectra were obtained on a Nippon Shimadzu Qp-1000 GC-MS Spectrometer. Elemental analyses were carried out on a Carlo Erba-1106 instrument. Microwave irradiation was carried out in a modified Galanz WP 750B commercial microwave oven at 2450 MHz. Melting points were determined with an electrothermal micromelting point apparatus and are uncorrected.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

General procedure for the synthesis of 2-aroyl-3,5-diarylfuran: Under a nitrogen atmosphere, $BF_3{\cdot}OEt_2$ (15 mmol) was added to a mixture of aromatic aldehyde (6.25 mmol) and aromatic ketone (12.5 mmol) in anhydrous benzene (1 ml), which was then irradiated at 450W for 6–8 min. After the reaction, the dark red solution was cooled to room temperature and acetone (5ml) was added. Then the dark red solution was poured into Et_2O (250 ml). The yellow precipitate was filtered off, washed with Et_2O and dried with anhydrous Na_2SO_4 under vacuum. The dried 2,4,6-triarylpyrylium salt (5 mmol) was suspended in acetone (10 ml). A solution of Na_2CO_3 (2 mmol) and I_2 (2 mmol) in water (3 ml) was added, and the mixture also was irradiated at 450 W for 8-10 min. Then, the dark mixture was poured into a solution of $Na_2S_2O_3$ (20 mmol) in water (30 ml) and the aqueous phase was extracted with $CHCl_3$. The organic phase was washed with water, dried with anhydrous Na_2SO_4 and the volume was reduced under vacuum. The crude product was purified by column chromatography on silica gel using petroleum (b.p. 60–90°C) / ethyl acetate (v/v 10:1) as the eluent.

4a: M.p. 175–176°C; ^{1}H NMR ($CDCl_3$): δ=7.83–7.76 (d, 2H, *J*=8.6 Hz), 7.67–7.53 (m, 8H, *J*=7.2 Hz), 7.42–7.26 (m, 3H, *J*-6.2 Hz), 6.79(s, 1H); MS (*m/e,%*): 480 (M^+, 99), 325 (M^+-4-BrC_6H_4, 9), 183 (4-BrC_6H_4CO, 3) 155 (4-BrC_6H_4, 18.3); Anal. Cald. for $C_{23}H_{14}O_2Br_2$: C, 57.34; H, 2.93; found: C, 57.29; H, 2.84.

4b: M.p.162–163°C; ^{1}H NMR ($CDCl_3$): δ= 7.89–7.85 (d, 2H, *J*=6.8 Hz), 7.73–7.69 (d, 2H, *J*=6.6 Hz), 7.60–7.56 (M, 2H, *J*=9.6 Hz), 7.46–7.26 (m, 7H, *J*=8.2 Hz), 6.98–6.98(s, 1H); MS (*m/e,%*): 392 (M^+, 85), 281 (M^+-4ClC_6H_4, 11.4), 139 (4-ClC_6H_4CO, 37), 111(4-Cl C_6H_4, 30), 75 (C_6H_5, 14); Anal. Cald. for $C_{23}H_{14}O_2Cl_2$: C, 70.25; H, 3.59; found: C, 70.29; H, 3.59.

4c: M.p. 127–128°C; ^{1}H NMR($CDCl_3$): δ=8.00–7.95 (m, 2H, *J*=6.6Hz), 7.80–7.26 (m, 10H, *J*=6.4 Hz); 6.98–6.89 (m, 3H, *J*=7.2 Hz); 3.85–3.80 (s,3H); MS (*m/e, %*): 354 (M^+, 100) 247 (M^+-4-$OCH_3C_6H_4$, 4), 105 (4-$OCH_3C_6H_4$, 30), 103 (C_6H_5CO, 4), 77 (C_6H_5, 29); Anal. Cald. For $C_{24}H_{18}O_3$: C, 81.34; H, 5.12; found: C, 81.30; H, 504.

4d: M.p. 103–105°C; ^{1}H NMR($CDCl_3$): δ=7.94–7.89 (d, 2H, *J*=8.2 Hz), 7.69–7.61 (m, 4H, *J*=9.0 Hz), 7.27–7.23 (m, 4H, *J*=4.6 Hz), 6.95–6.89 (m, 3H, *J*=6.8 Hz), 3.84 (s,3H), 2.44–2.40 (d, 6H, *J*=6.8 Hz); MS (*m/e, %*): 382 (M^+, 100), 291 (M^+-4-$CH_3C_6H_4$, 7), 119(4-$CH_3C_6H_4CO$, 46), 91 (4-$CH_3C_6H_4$, 33); Anal. Cald. for $C_{26}H_{22}O_3$: C, 81.65; H, 5.79; found: C, 81.44; H, 5.99

4e: M.p.151–152°C; ^{1}H NMR($CDCl_3$): δ=8.03–7.98 (d, 1H, *J*=8.8 Hz), 7.83–7.48 (m, 8H), 7.29–7.25 (m, 2H, *J*=5.8 Hz); 6.79–6.90 (t, 2H, *J*=7.0 Hz), 3.85 (s, 3H); MS (*m/e, %*): 512 (M^+, 64), 185 (4-BrC_6H_4CO, 100), 155 (4-BrC_6H_4, 72), 76 (C_6H_4, 85); Anal. Cald. For $C_{24}H_{16}O_2Br_2$: C, 56.28; H, 3.15; found: C, 56.25; H, 3.14.

4f: M.p.163–164°C; ^{1}H NMR($CDCl_3$): δ=7.91–7.86 (m, 2H, *J*=8.6 Hz), 7.71–7.57 (m, 4H, *J*=7.4 Hz), 7.45–7.40 (m, 3H, *J*=8.8 Hz), 7.26 (s, 1H), 6.96–6.90 (m, 3H, *J*=4.3 Hz), 3.85–3.81 (s, 3H); MS (*m/e, %*): 422 (M^+, 88), 315 (M^+-4-$OCH_3C_6H_5$, 1), 311 (M^+-4-ClC_6H_5, 7), 139 (4-Cl C_6H_4CO, 100), 111 (4-ClC_6H_4, 98), 75 ($C_6H_4^+$, 52); Anal. Cald. for $C_{24}H_{16}O_3C_{l2}$: C, 68.10; H, 3.81; found: C, 68.01;H, 3.90.

4g: M.p.112–113°C; ^{1}H NMR($CDCl_3$): δ=8.09–7.95 (m, 4H, *J*=6.95 Hz), 7.64–7.35 (m, 10H, *J*=5.7 Hz), 7.26 (s, 1H); MS (*m/e, %*): 358 (M^+, 94), 111 (4-ClC_6H_4, 26), 105 (C_6H_5CO, 100), 77 (C_6H_5, 45); Anal. Cald. for $C_{23}H_{15}O_2Cl$: C, 76.99; H, 4.21 found: C, 76.55; H, 426.

4h: M.p.193–194°C; ^{1}H NMR($CDCl_3$): δ= 7.95–7.88 (m, 2H, *J*=8.6 Hz), 7.72–7.55 (m, 4H, *J*=7.7 Hz), 7.49–7.26 (m, 6H, *J*=7.4 Hz), 6.953 (s, 1H); MS (*m/e, %*): 426 (M^+, 72), 315 (M^+-4-ClC_6H_4, 15), 139 (4-ClC_6H_4CO, 100), 111 (4-ClC_6H_4, 77), 75 ($C_6H_4^+$, 28); Anal. Cald. for $C_{23}H_{13}O_2Cl_3$: C, 64.59; H, 3.06; found: C, 64.59; H, 3.31.

4i: M.p.194–195°C; ^{1}H NMR($CDCl_3$): δ=7.87–7.80 (m, 2H, *J*=8.8 Hz), 7.65–7.53 (m, 8H, *J*=6.1 Hz); 7.41–7.26 (m, 2H, *J*=6.8 Hz), 6.965 (s, 1H); MS (*m/e, %*): 516 (M^+2, 69.3), 361 (M^+2-4-BrC_6H_4, 15.3), 185 (4-BrC_6H_4CO, 100), 155 (4-BrC_6H_4, 73), 111 (4-ClC_6H_4, 9), 76 (C_6H_4, 45); Anal. Cald. for $C_{23}H_{13}O_2ClBr_2$: C, 53.47; H, 2.54; found: C, 53.47; H, 2.74.

4j:M.p. 154–155°C; ^{1}H NMR($CDCl_3$): δ=7.93–7.89 (d, 2H, *J*=8.4 Hz), 7.69–7.57 (m, 4H, *J*=6.0 Hz), 7.39–7.24 (m, 6H, *J*=5.0 Hz), 6.90 (s, 1H); 2.44–2.41 (d, 6H, *J*=7.6 Hz); Ms (*m/e, %*): 386 (M^+, 46), 119 (4-$CH_3C_6H_4CO$, 72), 111 (4-ClC_6H_4, 15), 91 (4-$CH_3C_6H_3$, 100), 76 (C_6H_4, 8), 65 (C_4HO, 46); Anal. Cald. for $C_{25}H_{19}O_2Cl$: C, 77.62; H, 4.95; found: C, 77.76; H, 4.98.

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