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SYNTHESIS OF BIS(SUBSTITUTED BENZYLIDENE)CYCLOALKANONE USING SUPPORTED REAGENTS AND MICROWAVE IRRADIATION

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SYNTHESIS OF *BIS*(SUBSTITUTED BENZYLIDENE)CYCLOALKANONE USING SUPPORTED REAGENTS AND MICROWAVE IRRADIATION

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ABSTRACT

Condensation of cycloalkanone with aromatic aldehyde and furfural using supported reagents to prepare *bis*(substituted benzylidene or furfurylidene)cycloalkanone in excellent yields under microwave irradiation.

Potassium fluoride has been used widely as a kind of base supported reagent in organic synthesis.^[1–3] Yamawaki and Ando found KF–Celite could catalyze an alkylating reaction in 1979.^[4] Further, they found Al_2O_3 was the most efficient one to enhance reactivity of KF among common solid supports, such as silica gel, montmorillonite and clay.^[5,6] Moreover, Yamawaki et al. were the first to use KF–Al₂O₃ in Knoevenagel condensation under conventional conditions.^[7] However, many of the reaction needed a

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long time and gave a low yield. Microwave irradiation has found a lot of applications in recent years.^[8–12] The reaction time can be shortened greatly under microwave irradiation, so it is a new and convenient synthetic method.

In this paper, we wish to report a very simple and convenient synthesis of *bis*(substituted benzylidene or furfurylidene)cycloalkanone by condensation cycloalkanone with aromatic aldehyde or furfural using $KF-Al_2O_3$ as an inorganic support under microwave irradiation conditions. The combination of microwave irradiation and supported reagents has been highlighted in recent years. The main advantages of the approach are shorter reaction time, minimum waste, high yields and the experimental ease of manipulation. Recovery of inorganic/catalyst is generally possible. Here, we found the condensation reaction of aromatic aldehyde and cycloalkanone needs only 5 min. The yields of the products are good. The reactions are shown in Scheme 1 and the results are summarized in Table 1.

RESULTS AND DISCUSSION

Taking the reaction of benzaldehyde with cyclopentanone as an example, we investigate the effect of the supported reagents on the reaction. It was found that the activities of supported reagents are in the following sequence, respectively: $KF-Al_2O_3 > KF > K_2CO_3-Na_2CO_3 > K_2CO_3 > Na_2CO_3$. The results are summarized in Table 2.

We have also studied the effect of the power and time of microwave irradiation on the reaction. The results are summarized in Tables 3 and 4.

We also found that the reaction cannot be carried out if aliphatic aldehyde is used. To testify the selectivity of the reaction, we carried out the reaction in ratio (aromatic aldehyde/cycloalkanone) of 2:1 and 1:1.

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Table 1. Condensation Products of Cycloalkanone with Aromatic Aldehyde or Furfural Under Microwave Irradiation^{a,b,c}

No.	R	Ketone	Product	Yield (%)
3a	Н	Ļ	C ₆ H, C ₆ H,	73
3b	Н		C ₆ H ₅ C ₆ H ₅	83
3c	Н	Ů	C ₆ H ₃	80
3d	<i>p</i> -OCH ₃		P-CH ₃ OC ₆ H ₄ C ₆ H ₄ OCH ₃ -P	73
3e	<i>p</i> -OCH ₃		P-CH3OC ₆ H4-P	76
3f	p-Cl		P-CIC ₆ H ₄ Cl-P	80
3g	p-Cl		P-CIC ₆ H ₄ CI-P	81
3h	ОСНО			80
3i	ОСНО			82
3j	CH ₃ (CH ₂) ₅ CHO		no reaction	0
3k	CH ₃ (CH ₂) ₃ CHO	Ĵ	no reaction	0

^aIrradiation condition: power 750 W, time 5 min; KF-Al₂O₃ used as supported reagent.

^bmole ratio: aldehyde: 7cycloalkanone = 2:1.

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Table 2. Effect of the Supported Reagent on the Reaction^a

Supported Reagent	KF-Al ₂ O ₃	KF	K ₂ CO ₃ -Na ₂ CO ₃	K ₂ CO ₃	Na ₂ CO ₃
Yield ^b (%)	80	75	73	54	0

^aIrradiation condition: $T = 5 \min$, P = 750 W. ^bIsolated yield.

Table 3.	Effect of the Power	of MWI on	the Reaction ^{a,b}
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Power (W)	300	375	600	750
Yield ^c (%)	0	65	78	80

^aIrradiation time: 5 min.

^bKF–Al₂O₃ used as catalyst.

^cIsolated yield.

Table 4. Effect of the Time of MWI on the Reaction^{a,b}

Time (min)	2	3	5	7	8
Yield ^c (%)	0	74	80	75	68

^aIrradiation power: 750 W.

^bKF–Al₂O₃ used as catalyst.

^cIsolated yield.

Both the reaction provide the same product α, α' -bis(substituted benzylidene)cycloalkanone. α -mono(substituted benzylidene)cycloalkanone was not obtained.

EXPERIMENTAL

Microwave irradiation was carried out with a commertial microwave oven Glanz WP 750 B at 2450 Hz. IR spectra were measured for KBr discs using an Alpha Centauri FI-IR spectrophotometer. ¹H NMR spectra (80 MHz) were recorded in CDCl₃ using a PT-80 spectrometer or DRX-200. Spectrometer using tetramethylsilane as internal standard. Chemical shifts were expressed in ppm. Mass spectra were obtained on a Nippon

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Schimadzu QP-1000 GC-MS spectrometer. Melting points were determined with an electrothermal micromelting point apparatus and are uncorrected.

GENERAL PROCEDURE

 $KF-Al_2O_3$ (0.8 mmol) was added to a mixture of cycloalkanone (8 mmol) and aromatic aldehyde or furfural (16 mmol). The mixture was stirred and subjected to microwave irradiation in 750 W for 5 min. After the completion of the reaction, the mixture was filtered and washed with acetone immediately till the catalyst was white. Then the acetone was removed by evaporation. The pure sole product was obtained by recrystallization from ethanol or isolated by a short silica gel column using petroleum leve: ethyl acetate (10:1, v/v) as an eluent.

3a: M.p. 190–191°C (lit.,^[13] 189°C), IR ν (KBr): 3058, 3018, 1685, 1567, 1488, 930, 764, 687. ¹H NMR (80 MHz, CDCl₃): 3.12 (s, 4H), 7.6–7.01 (m, 12H). MS (*m*/*e*): 260 (M⁺).

3b: M.p. 118–118.5°C (lit.,^[14] 118°C), IR ν (KBr): 3078, 3023, 1660, 1572, 1485, 970, 771, 694. ¹H NMR (80 MHz, CDCl₃): 1.93–1.70 (m, 2H), 3.01–0.85 (m, 4H), 7.79 (s, 2H), 7.44–7.24 (m, 10H). MS (*m/e*): 274 (M⁺).

3c: M.p. 170°C (lit.,^[15] 172–175°C), IR ν (KBr): 3035, 2963, 2907, 1714, 1613, 765. ¹H NMR (200 MHz, CDCl₃): 1.97 (m, 2H), 3.02 (m, 2H), 7.57–7.24 (m, 8H). MS (*m*/*e*): 184 (M⁺).

3d: M.p. 214–215°C (lit., ^[16] 212°C), IR ν (KBr): 3030, 1666, 1596, 996. ¹H NMR (80 MHz, CDCl₃): 3.10 (s, 4H), 3.81 (s, 6H), 6.90 (d, 4H), 7.43 (d, 4H), 7.69 (s, 2H). MS (*m*/*e*): 320 (M⁺).

3e: M.p. 161–162°C (lit.,^[17] 162°C), IR v (KBr): 3005, 1658, 1593, 1558, 1480, 966. ¹H NMR (80 MHz, CDCl₃): 1.95–0.70 (m, 2H), 2.91 (t, 4H), 3.85 (s, 6H), 6.92 (d, 4H), 7.44 (d, 4H), 7.75 (s, 2H). MS (*m*/*e*): 334 (M⁺).

3f: M.p. 224–226°C (lit.,^[14] 225–226°C), IR ν (KBr): 3070, 1694, 1584, 1488, 983, 726, 685. ¹H NMR (200 MHz, CDCl₃): 3.091 (s, 4H), 7.628–7.263 (10H). MS (*m*/*e*): 225 (M-35).

3g: M.p. 146–147°C (lit.,^[18] 145–147°C), IR ν (KBr): 3050, 1690, 1583, 1488, 981. ¹H NMR (200 MHz, CDCl₃): 1.99–1.73 (s, 2H), 3.06 (s, 4H), 7.63–2.64 (m, 10H). MS (*m*/*e*): 307 (M-35).

3h: M.p. 164–165°C (lit.,^[19] 164°C), IR ν (KBr): 3135, 1681, 1625, 1600, 753. ¹H NMR (200 MHz, CDCl₃): 3.142 (s, 4H), 7.742–6.493 (m, 8H). MS (*m*/*e*): 240 (M⁺).

3i: M.p. 143–144°C (lit.,^[19] 145°C), IR ν (KBr): 3149, 1679, 1591, 1540, 751. ¹H NMR (200 MHz, CDCl₃): 1.93–1.71 (s, 2H), 3.08 (s, 4H), 7.78–6.42 (m, 8H). MS (*m*/*e*): 254 (M⁺).

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