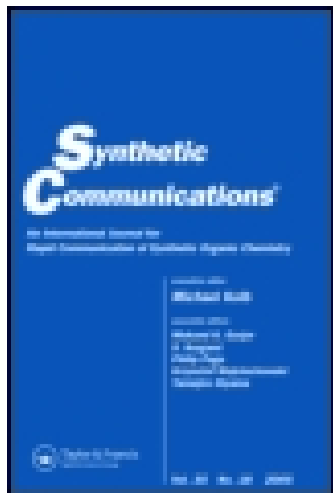


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Synthesis of Jasminaldehyde by solid-liquid phase transfer catalysis without solvent, under microwave irradiation

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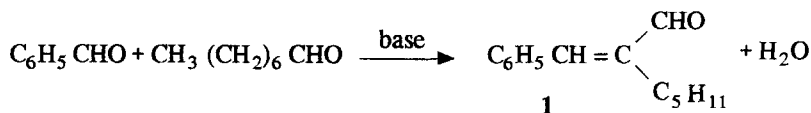
Abstract :

α -n-amylicinnamaldehyde (jasminaldehyde) was obtained with 82 % yield by solid-liquid phase transfer catalysis without solvent within 3 days at room temperature. By use of domestic microwave irradiation, the same yield was obtained within 1 minute at a power of 600 W.

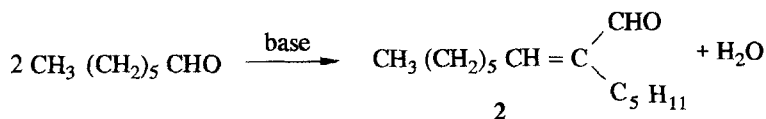
INTRODUCTION

α -n-amylicinnamaldehyde (jasminaldehyde) with violet artificial scent is used in perfumery compositions [1,2].

Jasminaldehyde **1** is obtained by aldol condensation of benzaldehyde with n-heptanal in basic media.



However the most important side product formed by self condensation of *n*-heptanal is 2-*n*-pentyl -2-*n*-nonenal **2**.



Another frequent competitive reaction is the Cannizzaro reaction promoted by reaction of a strong base (KOH, KOtBu) with benzaldehyde. Compounds **1** or **2** are mixtures of *Z* and *E* isomers.

In previous reports, **2** is obtained mainly by use of anions exchange resins (amberlite IR-4B) to initiate condensation. However, a mixture of **1** and **2** is obtained with cations exchange resins (IR 120) [3,4].

Afterwards, acetals of *n*-heptanal were used with ions exchange resins to avoid **2** formation. Unfortunately, yields in **1** are lower (yield % **1** = 37.5 with dibutyl acetal of *n*-heptanal) [5].

Nickel, cobalt, iron salts of carboxylic acids were also used with solvents under azeotropic distillation. For instance, with Fe-*n*-valerianate, yield % of **1** is 80 % (15 h, 190°C).

Finally, a short communication describes **1** synthesis with 80 % yield within 3 hours by solid-liquid phase transfer catalysis (PTC) (CH₂Cl₂, K₂CO₃, benzyl triethyl ammonium chloride) [7].

From previous reports, it appears that **1** synthesis is often tedious, sometimes with poor selectivity, complexity in experiments with large reaction times and high temperatures.

Solid-liquid PTC without solvent as well as mineral solid supports in "dry media" conditions were used in some reactions and gave good yields and better selectivity [9]. When compared to classical reactions performed in homogeneous solutions. These conditions were used for synthesis of **1**, and in some experiments coupled with microwave irradiation [8,9].

RESULTS AND DISCUSSION

Strong (KOtBu, KOH, NaOH) or weak bases (K₂CO₃, K₃PO₄) were used. Solid mineral supports like neutral alumina or basic alumina for aldol condensation [10]. Fontainebleau sand and Vietnam cap St Jacques sand were also used. Polymeric resin as amberlite XAD-2 precedently used in S_N2 reaction [11] was tested.

Table I

Reaction of n-heptanal (5 mmoles) with benzaldehyde (15 mmoles) by solid-liquid PTC without solvent at room temperature

Exp.	Base (mM)	transfer agent (mole %) ^a	t. (h)	% 1 ^b
1	K ₂ CO ₃ 10	0	48	22
2	" "	Aliquat 5	5	40
3	" "	" "	24	58
4	" "	" "	48	69
5	" "	" "	60	75
6	" "	" "	72	77 ^c
7	" "	" 25	60	82
8	" "	18-C-6 5	48	61
9	" "	TBA Cl 5	48	66
10	" "	TBA Br 5	72	72
11	" "	TBA HSO ₄ 5	72	75
12	KOH 0,5	Aliquat 5	24	70 ^d
13	" 5	" "	24	67
14	" "	" "	48	68
15	Na OH 5	Aliquat 5	48	20
16	Na OH 10	" "	48	28
17	KOtBu 5	Aliquat 5	48	31
18	K ₃ PO ₄ 10	Aliquat 5	72	69

a : % based on n-heptanal

b : Yields in isolated 1 by distillation are lower from 2 to 5 % to those evaluated by GC.

c : Yield % 2 : 9

d : Yield % 2 : 16

In solid-liquid PTC without solvent, NBu₄Br (TBABr), NBu₄Cl (TBACl), NBu₄HSO₄ (TBAHSO₄), Aliquat 336, 18-crown-6 were considered as transfer catalysts. Yields evaluated by GC with internal standard are reported in tables I, II and III.

Table II
Reaction of n-heptanal (5 mmoles) with benzaldehyde (15 mmoles)
in the presence of oxides or resins

Exp.	Base (mM)	PTC (mole %) ^a	Support	t. (h)	% 1
1	K ₂ CO ₃ 10	0	Sand ^b	48	12
2	" "	Aliquat 3	"	48	60
3	" "	" 5	"	48	74 ^e
4	" "	" 25	"	72	77
5	KOH 5	" 5	"	72	60
6	K ₂ CO ₃ 10	" 5	Alumina ^c	48	39
7	K OH 5	" 5	"	48	49 ^f
8	K OH 10	" 5	"	48	69
9	K ₂ CO ₃ 10	" 5	XAD-2 ^d	72	59 ^g

a : % based on n-heptanal

b : Fontainebleau sand (1.4 m²/g) or Cap St Jacques sand of Vietnam (2.3 m²/g)

c : Neutral activated alumina 90 (70 - 230 mesh Merck)

d : Amberlite XAD-2 (330 m²/g) (20 - 50 mesh Fluka)

e : Yield % 2 : 9 f : Yield % 2 : 19 g : Yield % 2 : 14

Table III
Reaction of n-heptanal (5 mmoles) with benzaldehyde (15 mmoles) under
microwave irradiation^a

Exp	Base (mM)	PTC (mole %) ^b	Power irradi. (Watts)	t. irradi. (mn)	T obtained (°C)	% 1	% 2
1	K ₂ CO ₃ 10	0	750	4	131	0	0
2	" 0.5	Aliquat 5	750	4	154	44	47
3	" 5	" 5	750	4	138	56	40
4	" 10	" 5	250	4	113	58	10
5	" "	" 5	350	4	141	75	15
6	" "	" 5	600	5	146	66	26
7	" "	" 25	350	4	125	71	8
8	" "	" 25	600	1	116	74	9
9	KOH 0.5	" 5	100	8	75	68	32
10	" "	" 5	350	4	104	56	44
11	" "	" 5	600	1	94	56	44
12	" "	" 25	100	4	86	71	26
13	" "	" 25	350	4	150	71	29
14	" "	" 25	600	1	118	82	18

a : domestic microwave Philips Whirlpool AT 5964 - Power restituted : 750 W

b : % based on n-heptanal.

1) Reactions under PTC conditions

The main part of PTC for anionic activation in those reactions is shown in tables I to III :

- in the absence of transfer agent, the yields of **1** are very low (yield % **1** : 22, table I ; yield % **1** : 12, table II ; yield % **1** : 0, table III) ;
- good yields of **1** are obtained with a weak base as K_2CO_3 and Aliquat 336 as catalyst. The best result (yield % **1** : 82, 60 h, room temperature) is obtained with K_2CO_3 and 25 % Aliquat 336 (table I, exp. 7), the quantity of side-product **2** being very low in these conditions.

This result constitutes an interesting improvement when compared to previous reports as it is obtained in the absence of solvent, with undeniable advantages in safety and cost and easier experimental work up.

2) Reaction on mineral or organic supports in "dry media"

The use of solid supports does not lead to any noticeable improvement in yields (table III). Alumina induces lower yields of **1** than sand (exp. 3-6). This can probably be due to the hydroxyl groups on alumina which are able to promote a Cannizzaro reaction with benzaldehyde, leading to benzylic alcohol formation [10].

3) Reaction under microwave irradiation

From results reported in table III, it appears that microwave irradiation favours crotonisation with **1** and **2** formation (exp. 2-14).

Excellent yields of **1**, with a good selectivity, are obtained with adequate power and time of microwave irradiation. Compound **1** is obtained with 75 % yield with K_2CO_3 and 5 % Aliquat 336 at 350 W (4 mn irradiation). 82 % of **1** are produced with KOH and 25 % Aliquat 336 at 600 W (1 mn irradiation) (exp. 5 and 14).

CONCLUSION

From this study it appears clearly that solid-liquid phase transfer catalysis without solvent is a good synthetic method to obtain jasminaldehyde **1**.

The results we obtained are an evident improvement when one compares to the previously reported results. Jasminaldehyde **1** is obtained with good yields with an important simplification in the work up and a good selectivity for this reaction.

On the other hand, excellent yields are obtained under microwave irradiation in very mild conditions as **1** is obtained with 82 % yield within 1 mn. This result underlines once more the excellent complementarity between PTC without solvent and microwave irradiation when anionic activation is involved [8,9,13-15].

EXPERIMENTAL

1) Chemicals

Chemicals are Merck, Janssen and Fluka products. Benzaldehyde and n-heptanal are distilled before use. Bases (K_2CO_3 , KOH, NaOH, K_3PO_4) are finely ground into powders. Mineral oxides, Fontainebleau sand, alumina, organic resins (amberlite XAD-2), ammonium salts are used without further purification.

2) General procedure

- *Synthesis of jasminaldehyde 1 by solid-liquid PTC without solvent or in "dry media" conditions :*

In a screw flask (30 ml) are introduced the transfer agent, benzaldehyde (15 mmoles), n-heptanal (5 mmoles) and the base impregnated or dispersed on solid support.

The mixture was shaken mechanically for 5 mn at room temperature. Organic compounds were extracted with 40 ml of diethyl ether by filtration on a column with Florisil (5 g) to eliminate ammonium salt and solid base. The solution was adjusted to 50 ml with diethyl ether and analyzed by GC.

- *Base impregnated support :*

Base was dissolved in water, then mineral oxide or organic resin was added and the mixture was stirred for 15 mn at room temperature.

Water was removed and the powder dried under vacuum (120°C, 24 h, 0.1 mmHg).

- *Synthesis of 1 under microwave irradiation :*

The reaction mixture is prepared as described in general procedure.

The open flask is introduced in a domestic microwave oven (Philips Whirlpool AT 5964 with an absorbed power = 1500 W, restituted power = 750 W). After microwave irradiation, the flask was cooled and the work up remained the same.

3) Analysis

Analysis were performed by GC with internal standard (benzyl benzoate) on an apparatus Carlo Erba GC 6000 Vega series with a capillary column OV1 (15 m). In some experiments, yields of **1** were evaluated by distillation under vacuum (1.5 mmHg).

Spectroscopic data for 1

By GC analysis, it appears that **1** (commercial or isolated product) is a mixture of E/Z isomers : 93/7.

Mass spectrometry $m/e = 41, 43, 77, 131, 145, 159, 173, 201, 202 (M^+)$

1H NMR (250 MHz), $CDCl_3$: δ (ppm) : 0,8 (3H, t) ; 1,25 (4H, m) ; 1,4 (2H, m) ; 2,45 (2H, t) ; 7,12 (1H, s) ; 7,45 (5H, m) ; 9,45 (1H, s). Coupling constant 4J between ethylenic proton and two allylic protons is not recorded (shift at 7.12 ppm without splitting for E isomer).

Spectroscopic data for 2

Compound 2 is exclusively the E isomer.

Mass spectrometry $m/e = 57, 71, 85, 125, 139, 153, 181, 210 (M^+)$

1H NMR (250 MHz), $CDCl_3$: δ (ppm): 0,8 (6H, m) 1,25 (12H, m); 1,40 (2H, m) 2,15 (2H, t); 2,25 (2H, m); 6,35 (1H, t); 9,25 (1H, s).. Coupling constant 4J between ethylenic proton and two allylic protons is not recorded (shift at 6.35 ppm, triplet, no splitting for E isomer).

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