

A synthetic route to 4-alkyl-αmethylhydrocinnamylaldehydes

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Abstract The 4-Alkyl- α -methylhydrocinnamylaldehydes (alkyl-isopropyl, isobutyl, methyl) are frequently used fragrances with desired floral (lilac, cyclamen, lily-of-the-valley) scent. These substances are valued for their good stability in basic solution and, therefore, are frequently used in soaps, detergents, or shampoos. These substances are synthesized by a two-step synthesis involving base catalyzed aldol condensation of 4-alkylbenzaldehyde with propanal followed by selective hydrogenation of the C=C bond. In aldol condensation, selectivity is decreased by formation of undesired products of propanal autocondensation 2-methylpent-2-enal. In this work the reaction conditions for homogenous catalyzed aldol condensation of 4-isobutylbenzadehyde with propanal were tested (catalyst type and amount, molar ratio of reactants, solvent type). Reaction conditions giving the best results (92% conversion, 79% selectivity) were adapted to other 4-alkyl-α-methylcinnamylaldehydes preparation with similar results. In the second step-hydrogenation of aldol product different types of catalyst (nickel, cobalt, palladium or Adkins catalyst), and also different solvents, were tested. Hydrogenation conditions leading to the highest yield (72% selectivity at 95% conversion) were adapted to other 4-alkylhydrocinnamyladehydes with similar results.

Keywords Cyclamen aldehyde · Silvial · Aldol condensation · Hydrogenation · 4-Alkyl-α-methylhydrocinnamylaldehyde

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Introduction

The 3-(4-isopropylphenyl)-2-methylpropanal (cyclamen aldehyde), 3-(4-isobutylphenyl)-2-methylpropanal (cyclamen homo aldehyde, Silvial) and 3-(4-methylphenyl)-2-methylpropanal (Jasmorange) are compounds widely used in, e.g., soaps, detergents, and shampoos because of their good stability in basic solutions and also in perfumes for their floral (lilac, lily-of-the-valley, cyclamen) and muguet notes. These fragrances are used to surrogate the frequently used cheap analogue of these compounds 3-(4-tertbutylphenyl)-2-methylpropanal (lily aldehyde), which has been classified as a possible mutagenic agent [1]. All mentioned compounds are synthesized by aldol condensation of propanal and appropriate 4-alkylbenzaldehyde followed by selective hydrogenation of a double C-C bond to corresponding 3-(4alkylphenyl)-2-methylpropanal (Fig. 1). The first step of aldol condensation is usually homogeneously catalyzed by inorganic hydroxides (NaOH, KOH) [2-4] or sodium methoxide [5], and this reaction gives the desired product but also a product of propanal autocondensation-2-methylpent-2-enal. The second step-hydrogenation, can be catalyzed by wide range of metal catalysts such as palladium supported on charcoal or alumina [4, 6–8], nickel catalyst [7–9] or rhodium catalyst [8].



Fig. 1 Aldol condensation of 4-alkylbenzaldehyde with propanal followed by hydrogenation of crossaldol condensation product [3-(4-alkylfenyl)-2-methylprop-2-enal (*a*); 2-methylprent-2-enal (*b*); 3-(4alkylphenyl)-2-methylpropanal (*c*); 3-(4-alkylphenyl)-2-methylprop-2-en-1-ol (*d*); 3-(4-alkylphenyl)-2methylpropan-1-ol (*e*)]

Hydrogenation gives three possible products— the desired 3-(4-alkylphenyl)-2methylpropanal, the undesired 3-(4-alkylphenyl)-2-methylprop-2-en-1-ol. and the product of subsequent hydrogenation of the desired product's carbonyl group 3-(4alkylphenyl)-2-methylpropan-1-ol. The 3-(4-Alkylphenyl)-2-methylprop-2-en-1-ol can be isomerized to the desired product [10].

The 3-(4-Alkylphenyl)-2-methylpropanal molecule is optically active. In all cases, R isomer is responsible for the pleasant scent, S isomer is described as a little musty [11]. The racemic mixture is used in applications due to economic reasons and also because the unfavorable smell of S isomer is almost entirely suppressed in the mixture. Nevertheless, some syntheses leading to non-racemic R isomer of cyclamen aldehyde have been reported in the past five years [11–13].

Results for aldol condensation of 4-*iso* propylbenzaldehyde with propanal were already reported by the authors [14]. Study of aldol condensation of 4-*iso* butylbenzaldehyde with propanal is not available in the literature; therefore, we performed detailed study of reaction conditions' influence on the reaction course. The goal was to get reaction conditions, which would be applicable to aldol condensation of different 4-alkyl substituted benzaldehydes with propanal. Usage of different palladium and nickel catalysts was also tested in aldol product hydrogenation.

Experimental

The 4-isopropylbenzaldehyde (Acros), 4-isobutylbenzaldehyde (TCI), 4-tertbutylaldehyde (Chemical Point UG), 4-methylbenzaldehyde (Sigma Aldrich), potassium and sodium hydroxide (Penta), sodium methoxide (Sigma Aldrich), methanol, ethanol, *n*-propylalcohol, *n*-butanol, *iso*propylalcohol, acetonitrile, *N*,*N*'-dimethylformamide, ethylacetate, and tetrahydrofurane (all solvents were from Penta) were used from commercial sources and used without further purification. Propanal (Sigma Aldrich) was freshly distilled before reaction (b.p. 46 °C). Different palladium and nickel catalysts (Table 1) were used for hydrogenation.

Aldol condensation

In a typical experiment the flask was charged with the solvent and the catalyst, then 4-*iso*butylbenzadehyde (iBB) was added. The total amount of propanal was added dropwise to the mixture in three portions at the 0th, 30th and 60th min of the reaction. Except for monitoring the influence of temperature, all experiments were performed at room temperature (25 $^{\circ}$ C). When a higher temperature was used, the flask was equipped with a condenser. Samples were neutralized by acetic acid, diluted with ethanol, centrifuged and analyzed. At the end of the reaction, the reaction mixture was neutralized using acetic acid, washed with water, extracted using diethylether and evaporated.

Example of isolation of pure unsaturated aldehyde (forcyclamen aldehyde)

Reaction mixture was distilled using a laboratory rectification column filled with oriented packing Sulzer DX (efficiency 10 theoretical levels). The column was

Denotation	Туре	Name	Producer
K1	5% Pd/SiO ₂	Escat 1351	Stream chemicals
K2	3% Pd/C	K-0224	Heraeus
K3	5% Pd/ γ -Al ₂ O ₃	K-0251	Heraeus
K4	3% Pd/C	MPT3 W	Süd Chemie
K5	5% Pd/C	K-0227	Heraeus
K6	5% Pd/C	MPT5 W	Süd Chemie
K7	3% Pd/C	Noblemax 100	Süd Chemie
K8	3% Pd/C	Noblemax 100 T-4811	Süd Chemie
К9	3% Pd/C	Noblemax 100 T-4810	Süd Chemie
K10	70% NiO/SiO ₂	Nisat 320	Süd Chemie
K11	89% Ni, 9% Al, 2% Mn	Acticat 1200	Cattaloy
K12	83% NiO/SiO ₂	Nisat 330	Süd Chemie
K13	79% NiO, 3% ZrO ₂ /SiO ₂	Nisat 340	Süd Chemie
K14	18% CoO/Al ₂ O ₃	G6861	Süd Chemie
K15	47% CuO, 46% Cr ₂ O ₃ , 4% MnO, 22% BaO	G99B0	Süd Chemie
K16	74% NiO, 2% ZrO ₂ /SiO ₂	G69	Süd Chemie

Table 1List of usedhydrogenation catalysts

equipped with an electrically heated boiler. In order to prevent heat loss, the column mantle was also heated. Reflux ratio was set exactly (10–15). Rectification was carried out under low pressure (1.5–1.9 kPa). Fractions with boiling point were in the range of 137–138 °C and contained 97% of the desired forcylamenaldehyde.

Hydrogenation

Hydrogenations were performed in an autoclave (volume 160 ml; Parr). Fractions containing 80–97% of 3-(4-alkylphenyl)-2-methylprop-2-enal were used for hydrogenation. The autoclave was filled with an appropriate amount of catalyst (1 wt.% in case of Pd catalysts, 10 wt.% in case of other catalysts, Table 1), 10 g of 3-(4-alkylphenyl)-2-methylprop-2-enal and 90 ml of solvent, isopropylalcohol. Samples taken during the reaction were centrifuged and analyzed.

Both samples from aldol condensation and hydrogenation were analyzed using a Shimadzu GC 17A chromatograph fitted with a nonpolar column ZB-5 (60 m, 0.32 mm diameter, 0.25 μ m i.d. film) and FID. Composition of the reaction mixture was also monitored using a GC–MS Shimadzu 2010 fitted with a nonpolar column.

Results and discussion

Aldol condensation

Results for aldol condensation of 4-*iso*propylbenzaldehyde with propanal were already reported by the authors [14]. This reaction was performed under the following conditions: catalyst 33% methanolic solution of sodium methoxide, molar ratio 4-*iso*propylbenzadehyde:sodium methoxide:propanal 1:0.05:1, 25 °C, solvent methanol, 180 min of reaction (92% selectivity to forcyclamen aldehyde, 90% conversion of 4-*iso*propylbenzaldehyde, i.e., a 83% theoretic yield of desired product).

In aldol condensation of 4-*iso*butylbenzaldehyde (iBB) with propanal (PA), three catalysts were tested: sodium methoxide (reaction conditions used in [14] resulted in iBB conversion of about 50% in 5 h), sodium hydroxide (36% water and 19% methanolic solution) and potassium hydroxide (36% water solution). Because of higher iBB conversion (about 80% in 5 h) in case of inorganic hydroxides, only inorganic hydroxides were tested (Table 2, entry 1–10) in the following experiments.

Overall higher conversions at a comparable time of iBB were obtained using sodium hydroxide comparing potassium hydroxide. In both cases, iBB conversion (i.e., reaction rate) increased with increasing hydroxide amount in the range

Entry	Catalyst	Molar ratio catalyst:iBB	Molar ratio iBB:PA	iBB conversion (%)	Selectivity to cross-aldol product (%)
1	36% Water sol.	0.05:1	1:1.1	10	100
2	NaOH	0.075:1		88	91
3		0.1:1		92	86
4		0.15:1		76	94
5		0.2:1		83	92
6	36% Water sol. KOH	0.05:1		15	91
7		0.075:1		55	79
8		0.1:1		71	87
9		0.15:1		61	85
10		0.2:1		58	78
11	19% Methanolic sol. NaOH	0.1:1		66	87
12	36% Water sol.		2:1	93	75
13	NaOH		3:1	87	68

Table 2 Reaction results using different reaction conditions (methanol:iBB = 1:1 vol., 25 °C, 5 h,iBB = 4-isobutylbenzadehyde, PA = propanal)

0.05-0.1:1 (5 h). In the range 0.1-0.2:1, the initial reaction rate was higher with increasing amount of catalyst, but the total achieved conversion in 5 h was lower, due to the faster consumption of propanal by the autocondensation reaction. The products of the Canizzaro reaction of iBB (isobutylbenzoic acid), which could neutralize the catalyst, was not detected in the reaction mixture.

In this heterogeneous system (two liquid phases), the selectivity decreased with an increasing amount of water in the reaction mixture-it complicates the reactant transfer to catalyst. Due to the presence of a water solution of hydroxide, the reaction mixture consists of two phases that may limit the reaction rate; therefore, the usage of methanolic solution of sodium hydroxide was also tested (Table 2, entry 3 and 11, 19% concentration was caused by limited solubility of sodium hydroxide in methanol). In this case the selectivity to desired product remained the same (compared to the water solution), but the reaction rate was significantly lower (92% conversion in case of water solution vs. 65% conversion in case of methanolic solution). For all these reasons, sodium hydroxide water solution was chosen to be the catalyst in further reactions.

It should be mentioned that the only undesired product in the reaction mixture was formed by propanal autocondensation (2-methylpent-2-enal). This product decreased selectivity significantly as it was visible after testing the influence of the reactant molar ratio (Table 2, entry 3, 12-13) on reaction course. At the same conversion of iBB, the selectivity to desired product decreased with increasing PA amount in the reaction mixture due to the expected increased formation of 2-methylpent-2-enal. Initial reaction rate was increasing with increasing amounts of propanal.

Another tested reaction parameter was the influence of solvent type (Table 3) on the reaction course, relative yield was chosen to compare reaction results with different solvents. The highest relative yield was obtained using methanol; satisfactory results were also obtained using n-C2-C4 alcohols. Usage of other

Table 3 Influence of thesolvent type on reaction course $(36\%$ water solution of NaOH,NaOH: IBB: PA = $0.1:1:1.1$ molar, solvent:IBB = $1:1$ vol., $25 \ ^{\circ}C$, $5 \ h$)	Solvent	iBB conversion (%)	Selectivity to 2-methyl-3-(4- iso- butylphenyl)prop- 2-enal (%)	Relative yield (%)
	Water	19	44	8
	Methanol	92	86	79
	Ethanol	70	92	65
	n-Propylalcohol	72	94	67
	i-Propylalcohol	38	53	20
	n-Butanol	68	87	59
	Acetonitrile	44	72	32
	Ethyl acetate	5	75	4
	<i>N,N'</i> - Dimethylformamide	58	51	30
	Tetrahydrofurane	33	61	20
	None	57	65	37

solvents did not offer satisfactory results, which was probably influenced by solubility of NaOH in these solvents. In case of aprotic solvents, acetonitrile, tetrahydrofurane and the N,N'-dimethylformamide homoconjugation of sodium hydroxide occurred, which caused suppression of hydroxide protonation and dissociation [15]. In the case of these three solvents, hydroxide was probably present only in the water phase compared to other alcoholic solvents, where the dissociated hydroxide was present also in alcohol. Ethyl acetate was shown to be an inappropriate type of solvent, because it reacted with hydroxide and formed ethanol and sodium acetate. In the case of water, 4-*iso*butylbenzaldehyde conversion was very low and selectivity to desired product was also low, due to the faster formation of undesired 2-methylpent-2-enal.

The use of hydroxide as a catalyst was also tested in the case of other 4-alkyl substituted benzaldehydes with propanal (Table 4). It is obvious, that hydroxide can be successfully used as a catalyst in this reaction, although in the case of 4-*iso*propylbenzaldehyde, it could produce better results with sodium methoxide.

Hydrogenation

Hydrogenation of aldol condensation products was performed to obtain the desired fragrant product—saturated aldehyde (Fig. 2, I.). In this reaction a side product—unsaturated alcohol (II.) can occur. Both these products—saturated aldehyde (I.) and

Table 4 Results of aldol condensation of 4-alkylbenzaldehydes with propanal (36% water solution of
NaOH, NaOH:4-alkylbenzaldehyde:PA = 0.1:1:1.1 molar, methanol:4-alkylbenzaldehyde = 1:1 vol.,
25 °C, 5 h)

Substituent in <i>para</i> position	4-Alkylbenzaldehyde conversion (%)	Selectivity to 2-methyl-3-(4- alkylphenyl)prop-2-enal (%)	Relative yield (%)	
None	96	88	84	
Methyl	95	89	85	
<i>iso</i> propyl	91	83	76	
<i>iso</i> butyl	92	86	79	
<i>tert</i> butyl	87	83	72	



Fig. 2 Scheme of hydrogenation (R = methyl, *iso*propyl, *iso*butyl, *tert*butyl): saturated aldehyde (*I*.), unsaturated alcohol (*II*.), saturated alcohol (*III*.)

unsaturated alcohol (II.)— can occur following hydrogenation to saturated alcohol (III.). Reaction conditions strongly influence the final composition of the reaction mixture. According to the literature, palladium and nickel-based catalysts were chosen to perform these experiments.

To confirm that hydrogenation was heterogeneously catalyzed, the catalyst 83% NiO (K12, 120 °C, 8 MPa, solvent methanol) was chosen. Reaction was stopped after 60 min, depressurized and cooled to room temperature. The reaction mixture was removed from the autoclave, the catalyst was filtered and the reaction mixture was inserted back into the autoclave, pressurized and heated to desired temperature. No change in reaction mixture was observed after 60 min; therefore, we declared that the reaction was heterogeneously catalyzed. We also used atomic absorption spectroscopy to confirm that no nickel was leached into the reaction mixture during hydrogenation.

Influence of catalyst type

At first palladium catalysts were tested in hydrogenation (Table 5, entry 1-9) of 3-(4-isopropylphenyl)-2-methylprop-2-enal (forcyclamen aldehyde) to obtain the desired saturated aldehyde-cyclamen aldehyde. The maximal selectivity to the desired cyclamen aldehyde was the highest (61%) at 95% forcyclamen aldehyde conversion with Pd/Al_2O_3 catalyst (Table 5, entry 3), which was probably caused by the fact that this catalyst was the only one with Al₂O₃ support. Reactions catalyzed by other palladium catalysts possessed lower selectivity (Table 5, entry 1-2 and 4-9) and formation of subsequent saturated alcohol – cyclamen alcohol was higher. In the case of catalysts K4 and K6 (same catalyst producer) when using higher Pd loading, the reaction rate increased, on the other hand, the selectivity to cyclamen aldehyde decreased on the same conversion level (Table 5, entry 1-9). Acidity of the three types of used solid supports (active charcoal, SiO₂, Al₂O₃) strongly influenced hydrogenation result-the catalyst with the least acidic solid support-SiO₂ (K1), offered the best selectivity at 95% conversion. The catalyst supported on middle acidic solid support-SiO₂ (K1), gave the second best selectivity at 95% conversion. Hydrogenations catalyzed by catalyst with the most acid solid support-active charcoal (K5), resulted in the worst selectivities. K7, K8 and K9 were the catalysts offered by one producer with comparable properties that were confirmed in these experiments.

Other used catalysts were the catalysts with significantly lower activity comparing to palladium catalysts—nickel, cobalt or Adkins catalysts (Table 5, entry 10–16). With these catalysts, slightly higher selectivity to desired product was obtained—up to 67% selectivity to desired saturated aldehyde at 95% conversion (Table 5, entry 10–16). An exception was Adkins catalyst (Table 5, entry 15)—which preferably catalyzed hydrogenation to other intermediate—unsaturated alcohol (forcyclamen alcohol) with 68% selectivity at 95% conversion. In other cases saturated alcohol was the main product that decreased the selectivity. For comparison, a highly active Raney-nickel catalyst was also tested, but as it was assumed saturated alcohol was the main product of the reaction. In this case the

Entry	Catalyst	Catalyst amount (wt%)	Temp. (°C)	Pressure (MPa)	Solvent	Selectivity to cyclamenaldehyde (%)	
						at 50% FCA conversion	at 95% FCA conversion
1	5%Pd/SiO2(K1)	1	60	3	Methanol	48	44
2	3%Pd/C(K2)					43	39
3	5%Pd/Al2O3(K3)					60	61
4	3%Pd/C(K4)					37	37
5	5%Pd/C(K5)					44	42
6	5%Pd/C(K6)					28	23
7	3%Pd/C(K7)					50	33
8	3%Pd/C(K8)					50	31
9	3%Pd/C(K9)					42	26
10	70% NiO(K10)	10	120	8		76	66
11	Ra-Ni(K11)					0	8
12	83% NiO(K12)					80	67
13	79% NiO(K13)					82	53
14	18% CoO(K14)					78	45
15	Adkins(K15)					11	0
16	74% NiO(K16)					65	52
17	83% NiO(K12)				Hexane	70	57
18	83% NiO(K12)				1,4-Dioxane	86	67
19	83% NiO(K12)				Toluene	64	62
20	83% NiO(K12)				Tetrahydrofurane	78	66
21	83% NiO(K12)				1-Methoxypropanol	81	72
22	83% NiO(K12)				isopropylalcohol	80	67

Table 5 Forcyclamen aldehyde (FCA) results using different reaction conditions

decrease of catalyst amount to the level used in the case of rare metal catalysts (1 wt%) would decrease the reaction rate and increase the selectivity.

Influence of solvent type

Several types of solvents were used to perform the reaction using nickel catalyst (Table 5, entry 12 and 17–22). No straight trend concerning solvent polarity or basicity was observed. Resulting selectivities to desired cyclamen aldehyde ranged from 57 to 72% in 95% forcyclamen aldehyde conversion. The most significant difference was in the reaction time to reach 95% focyclamen aldehyde conversion (Table 6), which was probably caused simultaneously by different boiling point of solvents and hydrogen solubility in these solvents.

The reaction conditions for one palladium (3 MPa, 60 °C, *iso*propylalcohol, 1 wt% of catalyst 5% Pd-Al₂O₃ K-0251,) and one nickel catalyst (8 MPa, 120 °C, *iso*propylalcohol, 10 wt% of catalyst NISAT 330) were chosen to perform reactions (Table 7) with other 3-(4-alkylphenyl)-2-methylprop-2-enals (alkyl = methyl,

E. Vrbková et al.

Table 6 Time to reach 95%forcyclamen aldehydeconversion using different	Solvent	ר כ	Time to 95% conversion (min)		
solvents	Hexan	1	195		
	1,4-Dioxan	2	290		
	Toluene		1	185	
	Tetrahydro	furan	2	225	
	1-Methoxy	propanol	1	125	
	isopropano	1	1	135	
	Methanol			95	
Table 7 Hydrogenetics results					
using different substrates	Metal type	Substituent in <i>para</i> position	Selectivity to unsaturated aldehyde (%)		
			50% conversion	95% conversion	
	Palladium	None	58	60	
		Methyl	56	61	
		<i>iso</i> propyl	60	61	
		<i>iso</i> butyl	62	59	
		<i>tert</i> butyl	57	58	
	Nickel	None	85	76	
		Methyl	90	79	
		<i>iso</i> propyl	80	67	
		<i>iso</i> butyl	81	76	
		<i>tert</i> butyl	78	66	

*iso*butyl, *tert*butyl) and with 3-phenyl-2-methylprop-2enal. In the case of palladium catalyst almost the same results (in the range of measurement error) were obtained for all substrates. In the case of nickel catalyst, the hydrogenation of methyl, *iso*butyl and non-substituted substrates resulted in slightly higher selectivity to desired product in comparison with *iso*propyl and *tert*butyl substituted substrates.

Conclusion

The first part of this work was dealing with aldol condensation of 4-*iso*butylbenzaldehyde and propanal giving desired 3-(4-*iso*butylphenyl)-2-methyl-prop-2-enal. The influence of several reaction conditions (e.g., catalyst type and amount, molar ratio, solvent type) was tested. The best result—92% 4-*iso*butylbenzaldehyde conversion and 79% selectivity to desired 3-(4-*iso*butylphenyl)-2-methylprop-2enal were obtained under the following conditions—solvent methanol, 36% water solution of NaOH, NaOH:iBB:PA = 0.1:1:1.1 molar, solvent:IBB = 1:1 vol., 25 °C, and 5 h. These conditions are applicable to aldol condensation of other 4-alkylsubstituted benzaldehydes with propanal. The second part of this work was dealing with hydrogenation of prepared 3-(4-*iso*propylphenyl)-2-methylprop-2-enal giving 3-(4-*iso*propylphenyl)-2-methylpropanal using several types of catalysts (nickel, cobalt or Adkins and palladium catalysts). Overall the best result—72% yield at 95% 3-(4-*iso*propylphenyl)-2-methylprop-2-enal conversion was obtained using 1-methoxypropanol as solvent (catalyst Ni-NISAT330, 8 MPa, 120 °C). Results of hydrogenation of other para substituted substrates showed that this way is adaptable to these substrates too.

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