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Solvent-free chelation-assisted intermolecular hydroacylation: effect of microwave irradiation in the synthesis of ketone from aldehyde and 1-alkene by Rh(I) complex

Chul-Ho Jun,[a,*] Jong-Hwa Chung,[a] Dae-Yon Lee,[a] André Loupy[b,*] and Saber Chatti[a]

[a]*Department of Chemistry, Yonsei University, Seoul 120-749, South Korea*
[b]*Laboratoire des Réactions Sélectives sur Supports, ICMO, CNRS UMR 8615, Bâtiment 410, Université Paris-Sud, 91405 Orsay Cedex, France*

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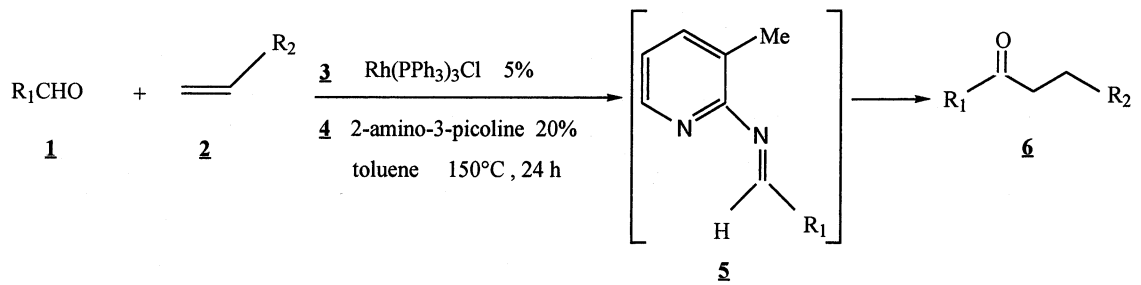
Abstract—As a green alternative to classical homogeneous catalyst in toluene in closed vessels, the intermolecular hydroacylation of 1-alkenes with aldehydes by Rh(I) complex (Wilkinson catalyst) can be realized efficiently under solvent-free conditions. When coupled to microwave activation, it results in a serious improvement when compared to classical conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Intermolecular hydroacylation is a useful synthetic method for obtaining ketones from aldehydes and olefins through C–H bond activation by transition metal complexes.[1–5] To suppress the decarbonylation that results in catalytically inactive metal carbonyl species, ethylene,[3] carbon monoxide,[4] or vinylsilane with a Co(I) catalyst[5] have been used. We have developed a general intermolecular hydroacylation of 1-alkenes using a Rh(I) complex and 2-amino-3-picoline **4** as a cocatalyst (Eq. (1)).[6] In this reaction, aldimine **5** is assumed to be the key intermediate, which suppresses decarbonylation as well as allows facile C–H bond activation through cyclometallation.[7]



(1)

Recently, we found that the reactivity in hydroacylation was improved when benzoic acid was added as a catalyst. Since the formation of aldimine **5** is supposed to be the rate determining step, the addition of benzoic acid, which catalyzes the condensation of aldehyde and **4** accelerates the overall rate of the chelation-assisted hydroacylation. Reactions can be now realized in toluene at 130°C within 4 h with high yields.[8]

As a new development and to operate under 'green chemistry' conditions, the reaction was next examined in the absence of solvent.[9] The effect of microwave (MW) activation was also studied as of noticeable interest under solvent-free conditions.

Two kinds of microwave equipments were used, either a domestic multimode oven or a more reliable monomode reactor with focused electromagnetic field and accurate control of temperature by infrared detection all along the reaction.[10] The main results are given in Table 1.

From Table 1, it is obvious to point out that hydroacylation of 1-alkenes with aldehydes can be considerably enhanced using solvent-free conditions, preferentially

* Corresponding authors. E-mail: junch@yonsei.ac.kr; aloupy@icmo.u-psud.fr

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Table 1. Intermolecular hydroacylation of 1-alkenes with aldehydes

1, R_1	**2**, R_2	Hydroacylated product **6** (%)[a]		
		Toluene 4 h 130°C[b]	Solvent-free MW	
			Domestic, 10 min [c]	Monomode
Ph	n-C_4H_9	66	75	–
	t-C_4H_9	63	69	–
	n-C_8H_{17}	22	38	95 (30 min)
	Me_3Si	87	83	–
	C_6F_5	75	80	–
	CH_2Ph	93	82	84 (10 min)
	⬡	71	85	–
n-C_6H_{13}	n-C_8H_{17}[d]	13[d]	0	61 (10 min)[d]

[a] Yield in isolated products.
[b] See Ref. 11.
[c] See Ref. 12.
[d] A 74% yield in aldolization product was isolated in the case of reaction in toluene and 37% for the solvent-free focused microwave-assisted reaction.

Table 2. Solvent-free hydroacylation of 1-alkenes with aldehyde for 30 min at 140°C

1, R_1	**2**, R_2	Reaction time (min)	Yield **6** (%)	
			Microwave	Conventional
Ph	n-C_8H_{17}	30	95	50
	CH_2Ph	10	84	30
n-C_6H_{13}	n-C_8H_{17}	10	61[a]	30[b]

[a] 37% of aldol product was formed.
[b] 13% of aldol product was formed.

under microwave irradiation. The improvement is even more important when using a monomode reactor due to wave focusing, which induces a better homogeneity in the electric field and subsequent need of a lower incident power. Such a beneficial effect of the monomode system was previously described[13] in some comparative experiments.

This new procedure involves safe conditions with noticeable improvements in reactivity, cost and energy reduction as well as simplicity of experimental conditions.

To check the possibility of intervention of specific (non-purely thermal) microwave effects, control experiments were done under the same conditions as under MW but under conventional heating inside a thermostated oil bath (Table 2).

A rather important non-thermal MW effect is here involved and leads to enhancements in yields. This effect is evident when one considers the difference in yields obtained under exactly the same conditions, including comparable profiles of raise in temperature for both kinds of activation (Fig. 1).

This MW specific effect is consistent with the fact that the rate-determining step of the reaction may be certainly the generation of aldimine **5** from aldehyde and 2-amino-3-picoline. As the transition state which develops a dipole (Scheme 1) is more polar than the ground state of the reaction, it results in a reduction of the activation energy due to enhanced dipole–dipole interactions with the electric field when the reaction is in progress.

In summary, we have presented here an alternative procedure to the classical homogeneous catalysis which is generally performed in toluene in closed vessels for

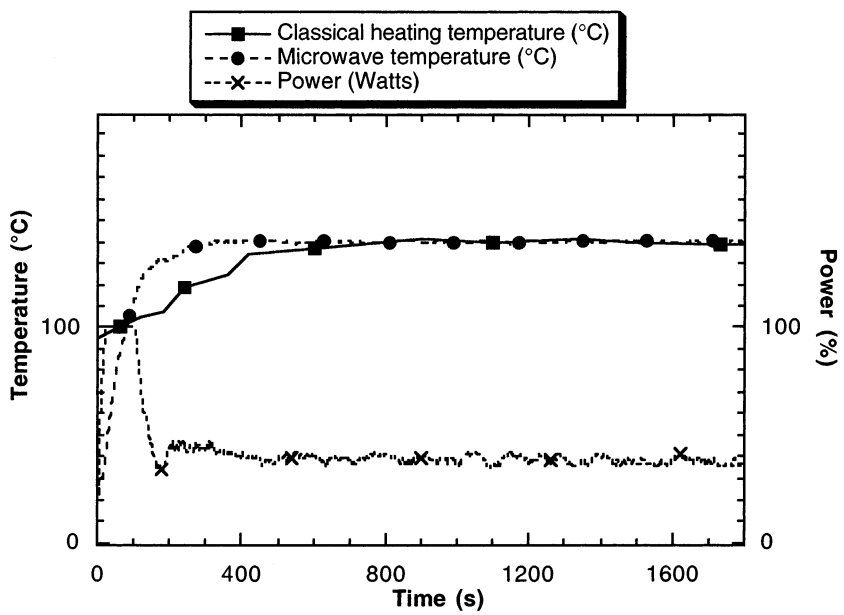
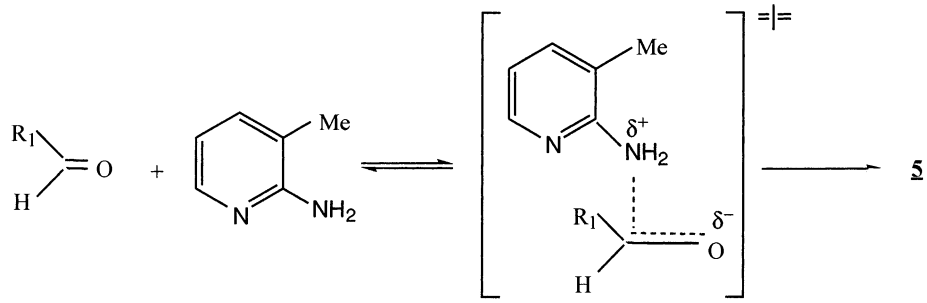


Figure 1. Profiles of raising in temperature for the reaction PhCHO+1-decene under microwave (●) or conventional heating (■).



Scheme 1. Evolution of the polarities during reaction progress.

rather long reaction times. This new efficient system (solvent-free reactions and microwave activation under 'green chemistry' conditions) can be used for intermolecular hydroacylation. Further work is in progress for the sake of generalization and directed toward a better understanding of this reaction.

Acknowledgements

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11. Typical procedure: Aldehyde (0.2 mmol), alkene (1.0 mmol), 2-amino-3-picoline (0.08 mmol), benzoic acid (0.02 mmol) and $RhCl(PPh_3)_3$ (0.01 mmol) were dissolved in toluene (100 mg) and then heated in the oil bath at 130°C (bath temperature) for 4 h. After the reaction, the product was purified by column chromatography.
12. Typical procedure: Aldehyde (0.2 mmol), alkene (1.0 mmol), 2-amino-3-picoline (0.08 mmol), benzoic acid (0.02 mmol) and $RhCl(PPh_3)_3$ (0.01 mmol) were mixed in the absence of any organic solvent and then submitted for 10 min to microwave irradiation inside a domestic microwave oven (Samsung, RE-431H, 700 W) or in a monomode Synthewave 402 Prolabo where power is enslaved to temperature at 140°C. After the reaction, the product was purified by column chromatography.
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