



Solvent-free Dehydration of Alcohols using LiCl-acidic Alumina

G. BAGHERI MARANDI¹, A. POURJAVADI^{2*} and H. HOSSEINZADEH³

¹Department of Chemistry, Islamic Azad University, Karaj Branch, P. O. Box 31485-313, Karaj, Iran.

²Department of Chemistry, Sharif University of Technology, Azadi Ave.,
P.O. Box 11365-9516, Tehran, Iran.

³Department of Chemistry, Payame Noor University, P.O. Box 19395-4697, Tehran, Iran.

*Corresponding author E-mail: purjavad@sharif.edu

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ABSTRACT

Conjugated enynes, dienes and simple olefins have been cleanly and selectively synthesized, good-to-excellent yields, by dehydration of corresponding alcohols using focused microwave irradiation on the surface of LiCl-acidic alumina.

Key words: Conjugated enynes, Dehydration, Microwave, Alumina, Solvent-free.

INTRODUCTION

During recent years, the microwave irradiation in conjunction with the solid supported catalysts was used to perform a wide range of organic reactions.^{1,2} The most advantages for these solvent-free microwave-assisted reactions are the high reaction yields, improvement in reaction selectivity, remarkable practical and handling simplicity, decreasing in reaction rate and without the need for the solvents that are toxic and expensive. In addition, possibility of recovery of both products and supported reagents leading to an efficient and low waste route that achieve the societal, economic and environmental benefits.

Alumina and its derivatives are the most widely employed supports, catalyst and reagents in organic syntheses, where surface of them

provides a polar environment and play an important role in this reactions.^{3, 4} Dehydration of alcohols is one of the reactions in that these supported inorganic reagents has been excessively used.⁵⁻⁷

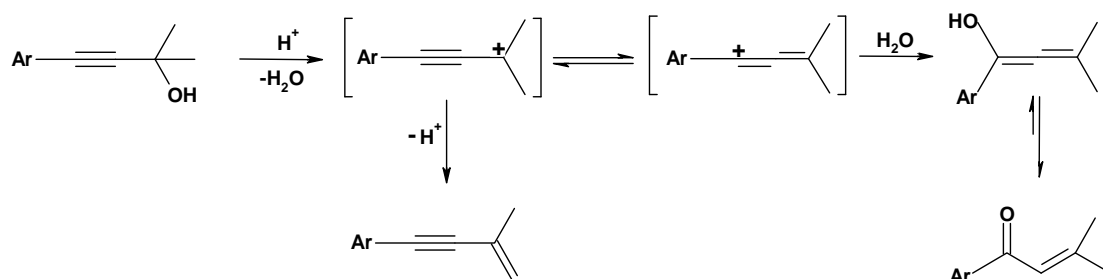
In this work, we report the synthesis of conjugated enynes and alkenes by dehydration of corresponding alcohols over LiCl-acidic Al_2O_3 ($LiCl \cdot H \cdot Al_2O_3$), a modified derivative of alumina as a supported reagent, under microwave irradiation.

Conjugated enynes are important materials that can be used in various fields such as cycloaddition reactions for construction of aromatic rings⁸, synthesis of the natural products⁹ and polymers.¹⁰ Sonogashira et al. for the first time reported the synthesis of conjugated enynes via palladium-catalyzed coupling of terminal alkynes with alkenyl halides.¹¹ After this report, many workers

modified the Sonogashira-coupling reaction and also suggested new synthetic approaches for preparation of conjugated enynes, ¹²⁻¹⁷ because of hardly synthesis of vinyl halides containing various functional groups. The dehydration of α -alkynols has also been used for synthesis of conjugated enynes using various reagents such as Tin (II) chloride in 1,3-dimethylimidazolidin-2-one, ¹⁸ zeolite catalyst¹⁹ and polyphosphoric acid trimethylsilyl ester.²⁰

In the previous works, we reported synthesis of conjugated enynes selectively via dehydration of α -aryalkynols using classical

heating method²¹ and also using p-TsCl/natural alumina under classical and microwave heating methods.²² In this paper, microwave-assisted dehydration of several α -aryalkynols, and a number of other alcohols was performed by using the LiCl-H₂O₃ solid supported reagent. Representative results are shown in Table 1. α -Aryalkynols, 1A-8A, were synthesized using Sonogashira reaction,^{11,23} are selectively converted to the corresponding conjugated enynes, 1P-8P, in good yields, in comparison to α - β -unsaturated carbonyl compounds that can be obtained via Meyer-Schuster rearrangement²⁴ (Scheme 1).



Scheme 1:

The other alcohols, 9A-16A were also converted to the corresponding alkenes at the same method, in good to excellent yields.

It is obvious that alkenols, in acidic media, were converted to conjugated dienes. Therefore,

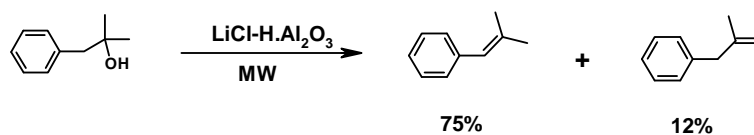
the alkenol 14A, in LiCl-H₂O₃ media, was selectively converted to the corresponding conjugated diene 14P, via rearrangement of the resulted carbocation (Scheme 2).



Scheme 2:

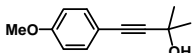
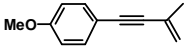
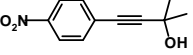
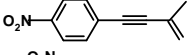
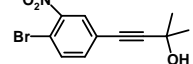
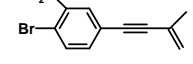
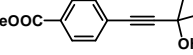
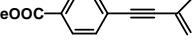
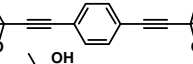
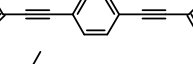
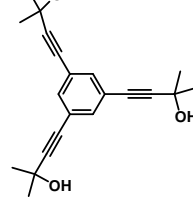
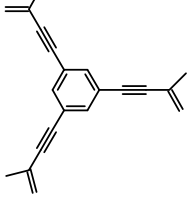
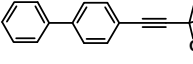
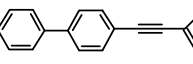
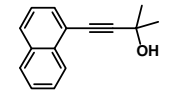
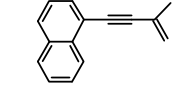
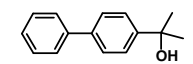
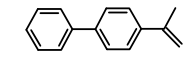
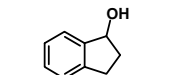
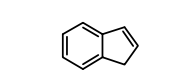
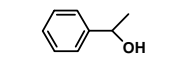
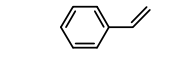
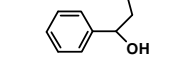
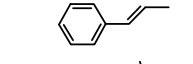
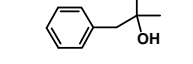
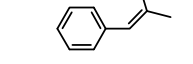
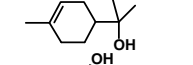
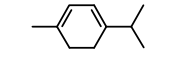
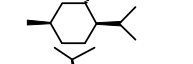
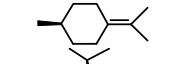
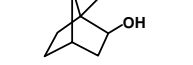

Also, conjugated alkene 13P is the major product of the dehydration of homobenzylic alcohol

13A (Scheme 3).



Scheme 3:

Table 1: Dehydration of alcohols using microwave irradiation on the surface of LiCl-acidic alumina

Entry	Alcohol (A) ^a	LiCl (g)	H ₂ Al ₂ O ₃ (g)	Time (min)	Temp. (°C)	Product (P)	Yield (%) ^b	M.P.(°C) or phys. state	Lit. M.P.(°C) or phys. state
1		0.12	2	6	105		80	Yellow liq.	(Yellow liq.) ²²
2		0.15	2	7	120		85	95.5-96.5	(95.5-96.5) ²²
3		0.2	2	7.5	140		75	50-51	(50-51) ²²
4		0.15	2	7.5	120		75	62-63	(62-63) ²²
5		0.25	3	4	120		85	97.5-98.5	(97.5-98.5) ²²
6		0.4	3	8	135		70	71.5-72.5	(71.5-72.5) ²²
7		0.12	2	3.5	90		85	69.7-70.5	
8		0.12	2	3	95		80	Yellow liq.	
9		0.12	2	3	90		90	121.2-122.7	
10		0.12	2	3	80		85	Yellow liq.	(Yellow liq.) ²⁵
11		0.12	2	3	85		83	Colorless liq.	(Colorless liq.) ²⁶
12		0.12	2	3	80		85	Yellow liq.	(Yellow liq.) ²⁷
13		0.12	2	5	100		75	Yellow liq.	(Yellow liq.) ²⁸
14		0.12	2	4	95		91	Yellow liq.	(Yellow liq.) ²⁹
15		0.12	2	5	100		86	Yellow liq.	(Yellow liq.) ³⁰
16		0.12	2	6	110		92	108.5-111	(109-110) ³¹

^a The physical and/or spectroscopic data of arylalkynols, **1A-8A**, was reported in the previous work²² and for other alcohols corresponded exactly to those cited in literature. ^b Determined by GC.

In our procedure, the alkanol 15A was converted to the more substituted alkene 15P (Scheme 4).

In conclusion, herein we reported a simple, coefficient and fast method for the preparation of conjugated enynes, dienes and simple olefinic compounds via dehydration of corresponding alcohols using $\text{LiCl}\cdot\text{H}\cdot\text{Al}_2\text{O}_3$ under MW irradiation.



Scheme 4

EXPERIMENTAL

The acidic Al_2O_3 used Aluminium oxide 90 active acidic (Merck-1078). Column-chromatographic separations were performed on silica gel 60 (Merck-9385). Thin-layer chromatography (TLC) was performed on silica gel 60 (Merck-7748) plates and visualisation was effected with short wavelength UV light (254 nm). Melting points were obtained on a Buchi B-540 melting point apparatus. MW experiments were performed in a Westinghouse 1400 W (900 W output) domestic MW oven. The arylalkynols were prepared using the Sonogashira reaction and the other alcohols were analytical grade.

General procedure for the microwave-assisted synthesis of conjugated enynes and alkenes

The certain amounts of LiCl and acidic alumina (indicated in Table 1) were well mixed and then 1 mmol of alcohols was added into the mixture and the mixture was grind using a pestle and mortar. The mixture was poured into a 200 mL Erlenmeyer flask attached to a short column (12x2cm) and was irradiated by microwave with level 10 (high power-900W) for certain time according to Table 1. Then the mixture was cooled to room temperature and the product was extracted with ethyl acetate. After this, the solvent was removed *in vacuo* to afford a crude product. Finally, the purified product was obtained by column chromatography using hexane as eluent.

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