

1,8-Dioxo-Decahydroacridines Synthesis Using a Maghnite-H⁺ Clay as Acid Eco-Friendly Catalyst

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ARTICLE INFO**ABSTRACT**

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A simple and efficient approach for the synthesis of 1,8-dioxo-decahydroacridines 4a-f was proposed by multicomponent one-pot condensation of an aromatic aldehyde, 1,3-diketones and ammonium acetate in the presence of Maghnite-H⁺, an Algerian proton-exchange montmorillonite clay, as a green catalyst. Maghnite-H⁺ is an efficient, economical, recyclable and environmentally friendly catalyst. Its catalytic effect is considerable for the condensation reaction, with good to excellent yields in a short time.

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1. INTRODUCTION

In organic synthesis, researchers are always interested in the fastest synthetic methods. Indeed, multicomponent reactions (MCRs) offer the possibility of synthesizing new compounds from three reactants in a single step. This type of reaction (MCRs) constitutes a promising strategy in organic synthesis to produce bioactive molecules, because their synthesis is fast and efficient, without isolation of intermediates and in a single step.¹ The Hantzsch synthesis of 1,4-dihydropyridines (1,4-DHP) represents a typical example of a one-pot multicomponent reaction between an aldehyde, two equivalents of α -methylene such as ethyl acetoacetate or 1,3-cyclohexanedione and a nitrogen donor such as ammonium acetate. The first successful example of this reaction was reported in 1881 by Arthur Rudolf Hantzsch.²

Acridine derivatives constitute an important class of 1,4-dihydropyridines with a broad spectrum of potential biological and pharmacological activities, including: antibacterial and antimicrobial,³ anticancer,⁴ anti-inflammatory,⁵ antiviral, antimalarial, and antiallergic,^{6,7} mutagenic,⁸ antidiabetic,⁹ and antitumor activity in vitro and in vivo against various murine and human tumors.¹⁰ Acridine and its derivatives have also found industrial applications and are used in the production of dyes. Their excellent photophysical properties¹¹ make them ideal candidates for use as laser dyes.¹² Acridine and its derivatives are used as photosensitizers,¹³ and as photoinitiators in polymerization reactions.¹⁴ These molecules can exist in neutral, protonated, or deprotonated forms.¹⁵

Numerous methods have been described for the synthesis of these compounds, involving condensation between aldehydes, 1,3-diketone, and an amine, catalyzed by various compounds such as 2-hydroxyethylammonium acetate,¹⁶ [CMIM][HSO₄]¹⁷ L-proline,¹⁸ ZnO nanoparticles,¹⁹ CAN,²⁰ ρ -TsOH,²¹ Amberlyst-15,²² sodium 1-dodecanesulfonic acid (SDS),²³ 4-toluenesulfonic acid,²⁴ alginic acid,²⁵ In(OTf)₃,²⁶ [H-NMP]⁺[HSO₄]²⁷ TPANPs/PAA,²⁸ copper-doped ZnO,²⁹ sulfuric acid on silica,³⁰ ultrasound,³¹ ionic liquids,³² and microwave irradiation.³³

Each of these methods has limitations such as low yield, long reaction times, the use of large quantities of volatile organic solvents, and the complexity of some work-up procedures. Therefore, the development of new strategies for the synthesis of acridines, with advantages in terms of the use of less expensive and readily available catalysts or reagents, cleaner reactions, and simple product isolation, is of interest.

In this current work, we describe an environmentally friendly, simple, and highly efficient method for the synthesis of 1,8-dioxodecahydroacridine derivatives by reacting ammonium acetate with aldehydes and 1,3-dicarbonyls in the

presence of Magnite- H^+ .

The catalyst used in this study is a green, non-toxic, inexpensive, recyclable, and non-polluting montmorillonite clay called Maghnite- H^+ .³⁴ It has recently been used in the synthesis of bis-Schiff bases,³⁵ and in the synthesis of macromonomers and polymers by cationic polymerization.³⁶⁻³⁹ Maghnite- H^+ offers a potential new route for the synthesis of 1,8-dioxo-decahydroacridines with good to excellent yields.

2. EXPERIMENTAL MATERIALS

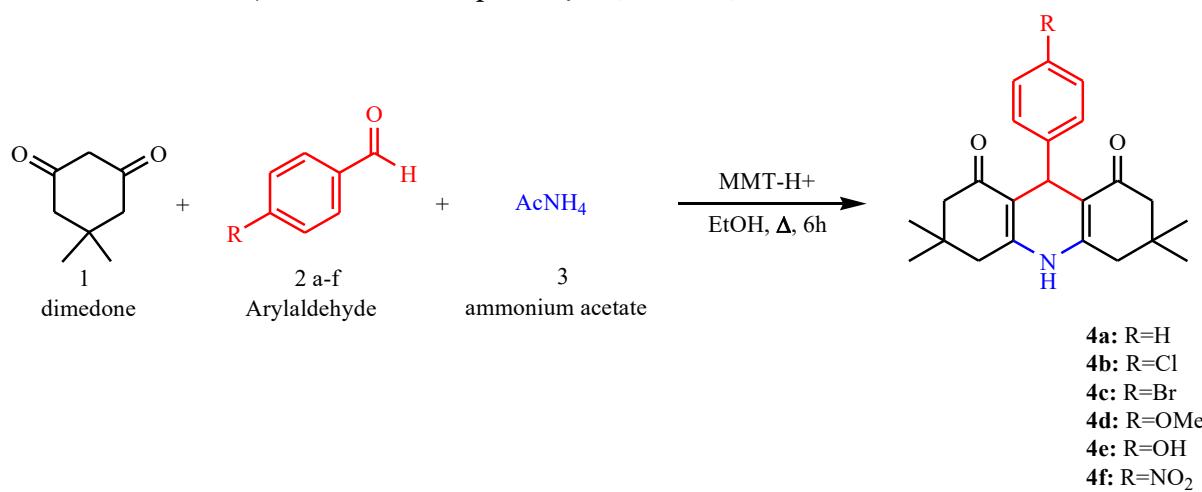
All chemicals were obtained from Biochem and sigma Aldrich and were used without further purification. Raw-Maghnite, Algerian montmorillonite clay was procured from "BENTAL" (Algerian Society of Bentonite). Thin layer chromatography (TLC) was done on silica gel TLC aluminium plates (E. Merck Kieselgel 60 F-254) and were visualized by exposure to UV-light at 254 nm or iodine vapor for few seconds. Melting point in °C was determined in open capillaries using Electrothermal melting point apparatus Stuart MPS-10. ¹H and ¹³C NMR spectra were acquired on a Bruker AQS-AVANCE spectrometer (400 MHz) at 25°C using DMSO-*d*₆ as solvent. Chemical shifts (δ) are reported in parts per million (ppm) relative to the internal standard tetramethylsilane (TMS, δ = 0.00 ppm).

2.1. General procedure for the preparation of Maghnite-H⁺ catalyst (MMT-H⁺)

The reaction was catalyzed by Maghnite- H^+ . It was prepared according to the following method: ^{40, 41} An amount of 20g of raw-Maghnite in powder form was dried for two hours at a temperature of 105°C to remove any traces of water. After drying, the Maghnite was put in an Erlenmeyer containing 500ml distilled water, then 0.23M sulfuric acid solution was added at once to the mixture Maghnite / water and agitated by a mechanical stirrer for about two days at room temperature. After that, the mineral part of the whole mixture was washed by distilled water until it becomes a free from sulfate and finally dried at 105°C for about 2hours.

2.2. General method for synthesis of 1,8-dioxo-dehydroacridines derivatives (4a-e)

To a mixture of dimedone **1** (2 eq), arylaldehyde **2a-f** (1 eq), and the ammonium acetate **3** (3 eq) in 10ml ethanol with catalytic amount of montmorillonite-H⁺ (10%). the reaction mixture was heated under reflux for the 4h. The progress of reaction is monitored by TLC. The crude product is dissolved with hot ethanol and then filtered to remove the solid catalyst. The filtrate is cooled to give the solid product. The resulting product is filtered, washed with ethanol and dried at 60-70°C to afford compound **4a-f** (Scheme 1).



Scheme 1. One-pot three compounds reaction for synthesis of 1,8-dioxo-decahydroacridines derivatives (4a-f) using Maghnite-H⁺

9-(phenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8-(2H, 5H)-dione (4a): yellow solid, (yield 87%), m.p: 260-262°C; ¹H NMR (400 MHz, DMSO-*d*₆, δ in ppm): 9.35 (s, 1H, NH), 7.41-7.23 (m, 5H), 4.78 (s, 1H), 2.76-2.45 (m, 4H), 2.11-1.82 (m, 4H), 1.11 (s, 6H), 1.02 (s, 6H); ¹³C NMR (100MHz, DMSO-*d*₆, δ in ppm) : 193.51, 152.87, 150.11, 126.15, 125.82, 123.10, 109.70, 50.34, 36.87, 27.27, 24.29, 20.40.

9-(4-chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4b):

yellow solid, (yield 94%), m.p: 297-299°C; ¹H NMR (400 MHz, DMSO-*d*₆, δ in ppm): 9.48 (s, 1H, NH), 7.32 (d, *J*= 8.2 Hz, 2H), 7.18 (d, *J*= 8.2 Hz, 2H), 4.58 (s, 1H), 2.59-2.47 (m, 4H), 2.12-2.07 (m, 4H), 1.09 (s, 6H), 0.92 (s, 6H); ¹³C NMR (100MHz, DMSO-*d*₆, δ in ppm) δ: 194.41, 149.50, 149.32, 147.17, 127.87, 127.80, 126.07, 111.94, 50.73, 33.10, 31.28, 29.36, 27.42.

9-(4-bromophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4c):

yellow solid, (yield 85%), m.p: 312-314°C; ¹H NMR (400 MHz, DMSO-*d*₆, δ in ppm): 9.52 (s, 1H, NH), 7.34 (d, *J*= 8.4 Hz, 2H), 7.25 (d, *J*= 8.4 Hz, 2H), 4.78 (s, 1H), 2.48-2.40 (m, 4H), 2.24-2.18 (m, 4H), 1.09 (s, 6H), 0.99 (s, 6H); ¹³C NMR (100MHz, DMSO-*d*₆, δ in ppm) δ: 194.41, 149.50, 149.32, 148.17, 127.62, 126.51, 125.27, 111.95, 50.77, 33.12, 31.44, 29.46, 27.52.

9-(4-methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4d):

yellow solid, (yield 92%), m.p. 275-277°C; ¹H NMR (400 MHz, DMSO-*d*₆, δ in ppm): 9.32 (s, 1H, NH), 8.22 (d, *J*= 8.2 Hz, 2H), 7.23 (d, *J*= 8.2 Hz, 2H), 5.04 (s, 1H), 3.66 (s, 3H), 2.39-2.28 (m, 4H), 2.04-1.97 (m, 4H), 1.05 (s, 6H), 0.94 (s, 6H); ¹³C NMR (100MHz, DMSO-*d*₆, δ in ppm): 195.12, 157.23, 149.96, 136.32, 128.20, 113.8, 54.9, 50.8, 41.51, 33.24, 33.15, 29.4, 28.69.

9-(4-hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4e):

yellow solid, (yield 90%), m.p: 284-286°C; ¹H NMR (400 MHz, DMSO-*d*₆, δ in ppm): 9.58 (s, 1H, NH), 7.75 (d, *J*= 8.2 Hz, 2H), 6.92 (d, *J*= 8.2 Hz, 2H), 5.62 (s, 1H), 4.82 (s, 1H), 2.60-2.49 (m, 4H), 2.32-2.21 (m, 4H), 1.14 (s, 6H), 0.99 (s, 6H); ¹³C NMR (100MHz, DMSO-*d*₆, δ in ppm): 194.98, 160.01, 151.48, 140.21, 132.66, 117.74, 113.04, 52.16, 41.18, 38.51, 35.41, 33.74, 28.70.

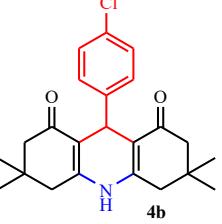
9-(4-nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydroacridine-1,8(2H,5H)-dione (4f): yellow solid, (yield 77%), m.p. 289-291°C; ¹H NMR (400 MHz, DMSO-*d*₆, δ in ppm): 9.76 (s, 1H, NH), 8.17 (d, *J*= 8.2 Hz, 2H), 7.42 (d, *J*= 8.2 Hz, 2H), 4.89 (s, 1H), 2.51-2.46 (m, 4H), 2.23-2.17 (m, 4H), 1.15 (s, 6H), 1.01 (s, 6H); ¹³C NMR (100MHz, DMSO-*d*₆, δ in ppm): 190.21, 181.60, 147.52, 146.12, 127.21, 123.52, 114.10, 111.21, 50.7, 33.65, 32.79, 30.14, 28.54.

3. RESULTS AND DISCUSSION

In this work, a green, non-toxic and recyclable catalyst was used for the synthesis of 1,8-dioxo-decahydroacridines derivatives (4a-f) by one-pot three compounds reaction (scheme 1).

To investigate the catalytic effect on the reaction yield, tests are carried out with different amounts of catalyst for the compound (4b). The results shown (Table 1) show that the use of 10% of catalyst at 79°C. Is the most effective and the yield obtained was 94% for 4 hours in ethanol (scheme 1).

Table 1. Catalytic effect on the one-pot synthesis of 1,8-dioxo-decahydroacridines derivatives (4a-e) catalyst by Maghnite-H⁺.

Entry	Cat (%)	Time(h)	T(°C)	Yield (%)
 4b	10	4	Reflux	93.96
	20			86.92
	30			79.32

Cat: Maghnite-H⁺

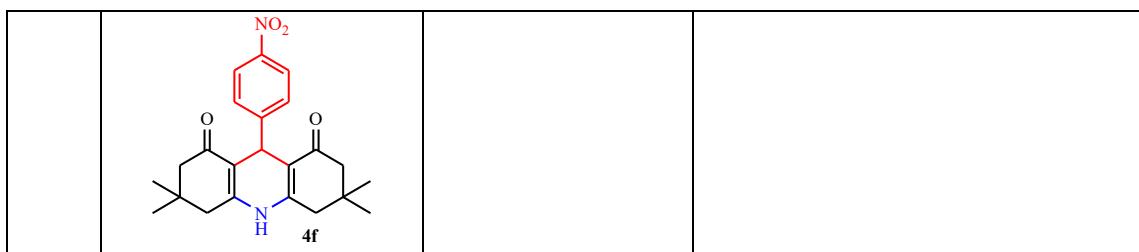
In general, 1,8-dioxo-decahydroacridine derivatives (4a-f) were obtained in good to excellent yields when mixtures

of dimedone 1, arylaldehyde 2a-f and ammonium acetate 3 containing 10% Maghnite-H⁺ were refluxed in ethanol for 4 hours (Table 2). The desired products precipitated after cooling the reaction mixture, and filtration yielded an analytically pure product. The experimental results (Table 2) obtained by this reaction show excellent yields compared to those in the literature.

The reaction mechanism for the synthesis of 1,8-dioxo-decahydroacridines derivatives **4a-f** is shown in (Scheme 2). The mechanism we propose for this transformation is based on the in situ formation of enaminone **B** derived from dimedone and ammonium acetate, the adduct of Knoevenagel **A** derived from dimedone and an aromatic aldehyde, followed by cyclization of intermediates **A** and **B**, followed by removal of a water molecule to give the products **4a-f**.

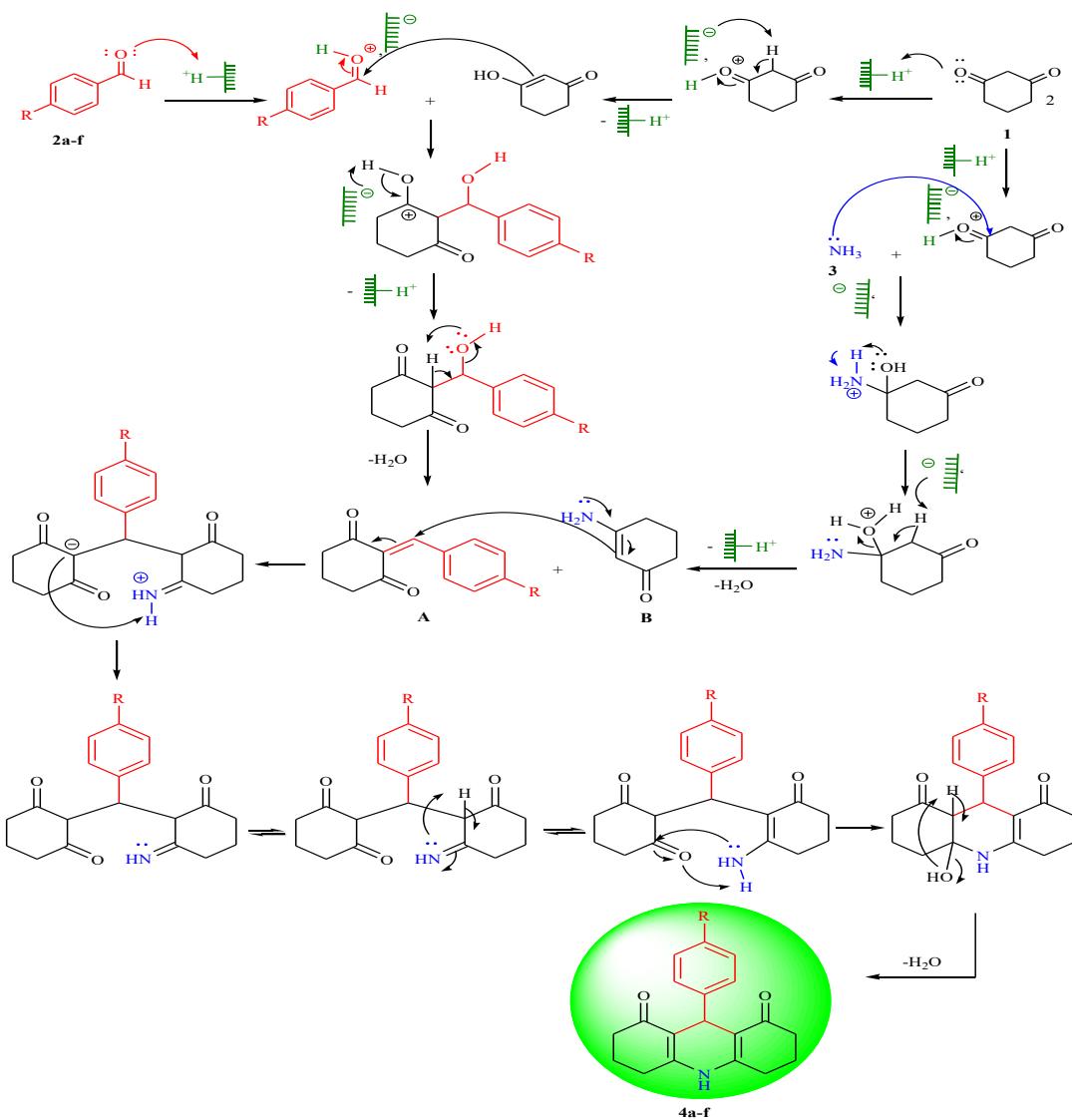
Table 2. One-pot synthesis of 1,8-dioxo-decahydroacridines derivatives (4a-f) catalyst by 10% of Maghnite-H⁺.

Entr y	Product	Yield* (%)		M.P. (°C)	
		Exp **	(Lit.)	Exp**	(Lit.)
1		87	85 [42]	260-262	290-291 [42]
2		94	95 [42]	297-299	299-302 [42]
3		85	88 [42]	312-314	313-315 [42]
4		92	85 [42]	275-277	276-278 [42]
5		90	75 [42]	284-286	303-305 [42]
6		77	75 [42]	289-291	284-286 [42]



(*) Isolated yield of product using montmorillonite-H+. The structure of products are determined by NMR and all spectral data are in good agreement with those of literature.

(**) Exp.: Experimental value (Lit.: literature value).



Scheme1. Proposed mechanism of the synthesis of 1,8-dioxo-decahydroacridines derivatives using Maghnite-H+

4. CONCLUSION

In conclusion, the one-pot three-component reaction of dimedone 1 with arylaldehyde 2a-f and ammonium acetate 3, in the presence of a catalytic amount of Maghnite-H+ in ethanol as solvent, constitutes an extremely efficient and chemoselective method for the synthesis of 1,8-dioxo-decahydroacridine derivatives. Moreover, Maghnite-H+ is a

non-toxic, inexpensive, and environmentally friendly catalyst. The products were obtained in good to excellent yield without further purification.

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