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Ultrasound-promoted synthesis of 4(3*H*)-quinazolines under $Yb(OTf)_3$ catalysis

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Dedicated to Prof. Jacek Mlochowski on the occasion of his 80th anniversary

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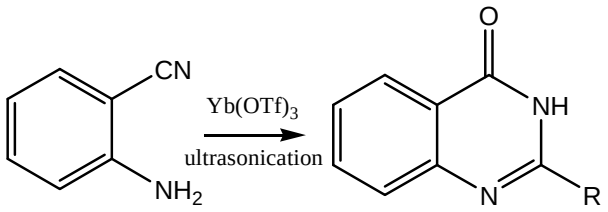
Abstract

A novel method to perform the Niementowski reaction leading to 4(3*H*)-quinazolines is reported. The 4(3*H*)-quinazolines were obtained in good to excellent yields by microwave irradiation or ultrasound-assisted synthesis from 2-aminobenzonitrile and acyl chlorides in solvent-free conditions and in the presence of $Yb(OTf)_3$ (10 mol%). Ultrasound-based methodology performed better than the microwave-assisted process in terms of yields for all examples. The procedure reported herein represents also the first reported example of an ultrasound-promoted Niementowski-like reaction.



87-98 %

Keywords: Catalysis, lanthanides, Niementowski reaction, 4(3*H*)-quinazolines, ytterbium triflate

Introduction

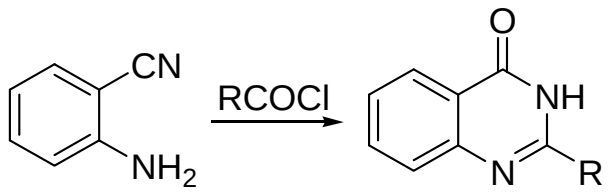
4(3*H*)-Quinazolines are a large group of naturally occurring and semisynthetic heterocyclic compounds. Up to now more than 120 alkaloids belonging to this class have been isolated and structurally characterized from natural sources: examples relevant to the present report include vasicinone and its biosynthetic derivatives from *Adhatoda* spp., rutaecarpine from *Evodia* spp., febrifugine from *Dichroa* spp., and several others.[1] Natural and semisynthetic 4(3*H*)-quinazoline derivatives are nowadays well known to possess a wide array of beneficial pharmacological effects, e.g. anti-cancer, anti-inflammatory, anti-microbial, anti-viral, anti-cholinesterase, and many others.[2] There are also many examples of drugs currently used in therapy having a quinazoline core and these include raltitrexed (marketed as Tomudex®), and methaqualone. A detailed survey and list of biologically active most relevant examples of 4(3*H*)-quinazolines have been recently reported in the literature.[3,4] 4(3*H*)-Quinazolines are also important synthons for the preparation of quinazolines, in turn representing interesting and promising bioactive molecules exerting a wide range of pharmacological effects.[5] Several synthetic methodologies for the preparation of 4(3*H*)-quinazolines have appeared in the literature. The recently published reviews by Guiry and coworkers[6] and by Wu and coworkers[4] cover reports to this concern up to the beginning of 2014.

Most recently these compounds have been obtained by the condensation of 2-aminobenzoate esters with formamide at 190-200 °C,[7,8] from *o*-nitrobenzamides by Pd-catalyzed hydrogenation (0.5 mol% Pd/C) in the presence of triethylammonium formate at 150 °C for 8 minutes under microwave irradiation,[9] from 2-aminobenzonitriles in a HCOOH/ H_2SO_4 conc. 20:1 mixture at 120 °C for 30 minutes,[5] from anthranilamides by $Y(OTf)_3$ catalyzed ring-closure and aerobic oxidation in DMSO at 110 °C after reaction with acyl chlorides,[10] and from anthranilamides by H_3P0_3 promoted condensation with β-dicarbonyl compounds in EtOH at 50 °C.[11] All the reported methods represent practical applications and modifications of the Niementowski reaction, originally described in 1894. The original protocol of this process suffered from harsh experimental conditions, low and non-reproducible yields of desired adducts, tedious work-up procedures, and co-occurrence of several side reactions. Improvements have been achieved by applying microwave irradiation under solvent-free conditions especially in terms of yields and shorter reaction times.[12,13]

Alternative methods to the use of substituted 2-aminobenzoates include the employment of 2-aminobenzonitriles as starting materials. The first example in this context was reported by Vanelle and coworkers who obtained the 4(3*H*)-quinazoline ring in two separate steps from the reaction of 2-aminobenzonitrile and chloroacetyl chloride under microwave irradiation at 150 W for 4 minutes in a pyridine/DMF mixture as the solvent, followed by cyclization of the intermediate amide promoted by urea hydroperoxide and K_2CO_3 at 500 W for 90 min.[14] A one-pot version of this last process has been reported by Hensbergen and coworkers, as cited above.[5] Although these Authors succeeded in obtaining the quinazoline ring in a single step, yields of desired adducts were generally low, being satisfactory only in three examples out of 11, and using different experimental conditions depending on the structure of the starting material and in general too severe both from the viewpoint of temperature (120 °C) and medium (mixture of concentrated acids as the solvent).[5] Thus, despite several methodologies to perform the Niementowski reaction being available, considering the importance of 4(3*H*)-quinazolines and their pharmacological potentialities, the development of milder and novel synthetic schemes to these compounds is a valuable, noteworthy, and useful task in organic and medicinal chemistry and surely represents a field of research of current and growing interest.

During the last two decades, rare earth salts have been shown to be efficient water-tolerant and recyclable Lewis acids. Trifluoromethanesulfonates of metals belonging to the lanthanide series in particular have been

seen to promote several carbon-carbon and carbon-heteroatom bond formation reactions in excellent yields often by means of a green chemical approach.[15] In continuation of our investigations aimed at settling easy to handle and practical protocols for the synthesis of building blocks and/or compounds of a potential pharmacological interest employing lanthanide triflates as catalysts, we describe here how 4(3*H*)-quinazolines can be efficiently obtained in good to very good yields by $Yb(OTf)_3$ hydrate catalyzed one-pot condensation of commercially available 2-aminobenzonitrile and differently substituted acid chlorides under solvent-free conditions using microwave irradiation (MW) or ultrasonication (US) (Scheme 1).



Scheme 1. The synthesis of 4(3*H*)-quinazolines by reaction of 2-aminobenzonitrile and acyl chlorides.

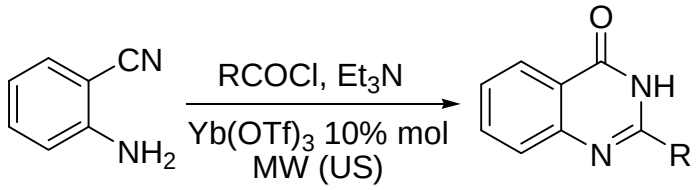
Results and Discussion

First trials were carried out using the above cited substrate (1.0 mmol) and acetyl chloride (2.0 mmol) as the acyl donor, in the presence of Et_3N (2.0 mmol) and $Yb(OTf)_3$ 5 mol% as the catalyst in a round-bottom flask at 120 °C for 30 minutes under solvent-free conditions. The reaction was monitored by thin layer chromatography (TLC). After the indicated time the complete disappearance of the starting benzonitrile was observed although a very complex unseparable mixture of products had been formed. We then decided to change parameters affecting the process but all modifications (e.g. shortening reaction times to 3 minutes, lowering the temperature to 70 °C, increasing catalyst load to 20 mol%) proved to be unsuccessful. In all cases several spots were detected on TLC or, as occurred for temperatures below 70 °C, the conversion of the starting material was largely incomplete.

We then decided to radically change experimental details and verify, using the same substrates and reagents, the efficiency of MW irradiation and US. After numerous attempts in terms of reaction times (from 1 to 15 minutes) and MW power values ranging from 100 W to 800 W (1 bar), the best conditions were assessed to be a MW power of 200 W (equivalent to a temperature of 80 °C), a reaction time of 6 minutes, and the presence of $Yb(OTf)_3$ hydrate 10 mol%.[16] Monitoring the process by TLC using these parameters revealed a complete conversion of the starting 2-aminobenzonitrile into a relatively pure product accompanied by only few minor spots. The crude mixture resulting from this step was diluted with Et_2O, the catalyst recovered by filtration, the filtrate washed twice with a 3% aq $NaHCO_3$ solution and then twice with a 5% citric acid solution, dried over $MgSO_4$ and evaporated to dryness under vacuum to provide a pure solid that was finally purified by SiO_2 gel column chromatography (eluent CH_2Cl_2/MeOH, 99.5:0.5). The desired 2-methyl-4(3*H*)-quinazoline (entry 1) was obtained in 72% yield. ^1H and ^{13}C NMR analyses confirmed the structure of the product. US-assisted synthesis was accomplished using the same mol% of $Yb(OTf)_3$ and operating for 45 minutes with the temperature of the water bath set at 40 °C. After the same work-up, 2-methyl-4(3*H*)-quinazoline was obtained in 95% yield without the need of any chromatographic purification (entry 1). In both experimental conditions a blank experiment carried out in the absence of $Yb(OTf)_3$ led to a very poor conversion of 2-aminobenzonitrile into the desired adduct (yield < 10%).

It is noteworthy that shorter reaction times resulted in an incomplete formation of 2-methyl-4(3*H*)-quinazoline while increasing the time, both under MW irradiation or US, led to major degradation of the final product as revealed by TLC analysis. Loading the catalyst at less than 10 mol% provided no satisfactory results in terms of yields, while an increase up to 20 mol% in both conditions did not significantly affect yields. Encouraged by results using acetyl chloride, we applied both MW irradiation and US to differently substituted acyl chlorides and the corresponding 2-substituted 4(3*H*)-quinazolines were synthesized in good to excellent yields as summarized in Table 1.

Table 1. $Yb(OTf)_3$ promoted synthesis of 4(3*H*)-quinazolines by microwave (MW) irradiation or ultrasonication (US)



Entry	R	Yield (%)[a]	
		MW	US
1	CH_3	72	95
2	Ph	61	98
3	Ph-CH=CH	64	91
4	$CH_3(CH_2)_{10}$	59	93
5	$CH_3(CH_2)_7CH=CH(CH_2)_7$	59	95
6	2-CH_3O-(C_6H_4)	62	92
7	2-F-(C_6H_4)	70	92
8	4-CH_3O-(C_6H_4)	71	89
9	3-NO_2-(C_6H_4)	72	94
10	$(CH_3)_2CH=CH$	65	92
11	cyclopropyl	73	87

[a] Yields of pure isolated products, characterized by ^1H NMR and ^{13}C NMR.

Differently substituted acyl chlorides (cyclic and acyclic aliphatic and unsaturated, aromatic with electron-withdrawing and electron-donating substituents attached to the benzene ring) reacted nearly to the same extent furnishing selectively the desired compounds in yields ranging from 59% to 73% in the case of MW irradiation and from 87% to 98% in the case of US. Blank experiments were also performed for all the acyl chlorides listed in the Table 1, each time providing yields < 10 %. In no cases, anthranilic acid, deriving from the hydrolysis of the nitrile function, or *N*-acylaminobenzonitriles were detected. Moreover potentially acid-sensitive moieties like the cyclopropane ring (entry 11), remained unaffected under both experimental conditions employed. $Yb(OTf)_3$ was recovered by filtration from each process, as described above. The catalyst could be reused for other reactions without significant loss of its activity. For example the reaction leading to 2-methyl-4(3*H*)-quinazoline (entry 1) was accomplished five additional times with the recycled Lewis acid providing the desired adduct in 71%, 71%, 72%, 68%, and 70% yields in the case of MW irradiation and 95%, 95%, 91%, 95%, and 94% in the case of US.

The same two processes were performed with other metal triflates belonging to the lanthanide series, namely Sc^{+3}, La^{+3}, Ce^{+3}, Eu^{+3}, Gd^{+3}, and Er^{+3}. Very limited conversion of 2-aminobenzonitrile was observed with La^{+3}, Ce^{+3}, Eu^{+3}, and Gd^{+3}, while Sc^{+3} and Er^{+3} providing yields lower than 30%. The greater efficiency of Yb^{+3} as the catalyst may be due to the fact that this cation is the "hardest" and thus most oxophilic in the lanthanide series due to its smaller ionic radius.[16] Indeed an example of 4(3*H*)-quinazoline synthesis promoted by $Yb(OTf)_3$ has been very recently reported in the literature.[17] However, in this work, Yoshimura and coworkers used anthranylamides as starting material and mesitylene as the solvent at 120 – 165 °C under an Ar atmosphere. Moreover $Yb(OTf)_3$ was used in a 20 mol% ratio without providing evidence of any easy and effective recycle and subsequent reuse of the catalyst. Our methodology is effective in avoiding the use of severe and harsh experimental conditions and more than stoichiometric loading of the catalyst and thus compares favourably to the already reported synthetic methodologies used to accomplish the title process. Moreover, to the best of our knowledge, the method described herein represent the first application of US to promote the Niementowski reaction.

Conclusion

We have demonstrated that differently substituted acyl chlorides undergo an efficient condensation reaction under the catalysis of $Yb(OTf)_3$ hydrate providing 2-functionalized 4(3*H*)-quinazolines using both MW irradiation and US, in good to excellent yields. The simple work-up procedure and mild conditions make our method a valid and alternative contribution in the field of quinazoline ring synthesis. Further investigations into the scope and other applications of $Yb(OTf)_3$ promoted reactions are now in progress in our laboratories and will be reported in due course.

Experimental Section

General. All reagents were obtained from Sigma-Aldrich Chemical Co and were used without further purification. All solvents were analytical grade. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200 (^1H NMR, 200 MHz; ^{13}C NMR, 50.32 MHz). $CDCl_3$ was used as the solvent and tetramethylsilane as an internal standard. Chemical shifts are reported in δ (ppm). Reactions were routinely monitored by TLC using Merck silica gel F_{254} plates. Melting points were measured on a Büchi melting point apparatus and are uncorrected. Elemental analyses were carried out on a Carlo Erba 1106 elemental analyser. The purity (> 98%) of commercial samples and final products was confirmed by TLC (Merck silica gel plates of type 60 F_{254}, 0.25 mm layer thickness) and combustion analysis. Microwave irradiation was carried out using a Monowave Edu (Anton Paar) apparatus (200 W, 5 min, 1 bar). Reactions were performed in an open reaction vessel. Ultrasonic assisted synthesis was accomplished using an Elma Transsonic T460/H apparatus.

General procedure for 4(3*H*)-quinazoline synthesis by microwave irradiation. An open reaction vessel containing a mixture of 2-aminobenzonitrile (1.0 mmol), acyl chloride (2.0 mmol), Et_3N (2.0 mmol), and $Yb(OTf)_3$ hydrate (0.1 mmol) was placed in the MW apparatus and irradiated at 200 W (80 °C) for 6 min. The reaction was monitored by TLC (eluent CH_2Cl_2/MeOH, 99:1). The crude solid obtained was diluted with Et_2O and the resulting suspension filtered under vacuum to separate the catalyst, then the precipitate washed several times with Et_2O. The filtrate was washed twice with a 3% aq $NaHCO_3$ (10 mL) and then twice with a 5%

citric acid solution (mL), dried over $MgSO_4$ and evaporated to dryness under vacuum to provide a solid that was finally purified by SiO_2 gel column chromatography (eluent CH_2Cl_2 / MeOH 99.5:0.5) yielding the desired product.

General procedure for 4(3*H*)-quinazolines synthesis by ultrasonication. The same general procedure as above was used, but without purification by SiO_2 column chromatography, but with a 45 minute ultrasonication and in a bath temperature of 40 °C.

2-Methyl-4(3*H*)-quinazoline (entry 1). Pale yellow solid, mp 176 – 177 °C. Yield 72% (MW), 95% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[18] Anal. Calcd. for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49; O, 9.99. Found: C, 67.47; H, 5.07, N, 17.45; O, 9.96.

2-Phenyl-4(3*H*)-quinazoline (entry 2). Pale yellow solid, mp 121 – 122 °C. Yield 61% (MW), 98% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[18,19] Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.60; O, 7.20. Found: C, 75.66; H, 4.53, N, 12.63; O, 7.18.

2-(2-Phenylethenyl)-4(3*H*)-quinazoline (entry 3). Yellow solid, mp 322 – 323 °C. Yield 64% (MW), 91% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[20] Anal. Calcd. for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28; O, 6.44. Found: C, 77.37; H, 4.88, N, 11.31; O, 6.42.

2-Undecyl-4(3*H*)-quinazoline (entry 4). Pale yellow waxy solid. Yield 59% (MW), 93% (US). ^{1}H NMR: δ 0.92 (t, 3H, *J* 7.5 Hz), 1.18-1.76 (m, 18H), 2.57 (t, 2H, *J* 7.4 Hz), 7.21 – 7.87 (m, 4H); ^{13}C NMR: δ 14.3, 14.9, 22.6, 24.0, 27.8, 29.8, 29.9, 32.1, 34.3, 36.2, 37.5, 121.1, 126.7, 127.0, 134.8, 148.8, 156.8, 163.9, 173.1. Anal. Calcd. for $C_{20}H_{30}N_2O$: C, 76.39; H, 9.62; N, 8.91; O, 5.09. Found: C, 76.41; H, 9.61, N, 8.88; O, 5.07.

2-(Eptadec-*cis*-8-enyl)-4(3*H*)-quinazoline (entry 5). Pale yellow waxy solid. Yield 59% (MW), 95% (US). ^{1}H NMR: δ 0.93 (t, 3H, *J* 7.5 Hz), 1.08-1.42 (m, 20H), δ 1.62-1.79 (m, 2H,), 1.92-2.04 (m, 2H), 2.41-2.48 (m, 2H), 5.23 (s, br, 1H), 7.02-8.24 (m, 4H); ^{13}C NMR: δ 14.3, 23.1, 25.8, 27.0, 28.9, 29.0, 29.1, 29.2, 29.3, 29.5, 29.6, 29.9, 30.0, 32.1, 38.0, 116.1, 124.0, 129.8, 130.1, 130.2, 132.8, 132.9, 134.0, 141.5, 172.2. Anal. Calcd. for $C_{25}H_{38}N_2O$: C, 78.48; H, 10.01; N, 7.32; O, 4.18. Found: C, 78.43; H, 9.99, N, 7.31; O, 4.16.

2-(2-Methoxyphenyl)-4(3*H*)-quinazoline (entry 6). Yellowish solid, mp 210 – 211 °C. Yield 62% (MW), 92% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[21] Anal. Calcd. for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10; O, 12.68. Found: C, 71.45; H, 4.77, N, 11.13; O, 12.71.

2-(2-Fluorophenyl)-4(3*H*)-quinazoline (entry 7). Pale yellow waxy solid. Yield 70% (MW), 92% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[22] Anal. Calcd. for $C_{14}H_9FN_2O$: C, 69.99; H, 3.78; N, 11.66; O, 6.66. Found: C, 70.02; H, 3.79, N, 11.69; O, 6.64.

2-(4-Methoxyphenyl)-4(3*H*)-quinazoline (entry 8). Yellow solid, mp 200 – 202 °C. Yield 71% (MW), 89% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[23] Anal. Calcd. for $C_{15}H_{12}N_2O_2$: C, 71.42; H, 4.79; N, 11.10; O, 12.68. Found: C, 71.43; H, 4.79, N, 11.11; O, 12.69.

2-(3-Nitrophenyl)-4(3*H*)-quinazoline (entry 9). Yellow solid, mp 350 – 351 °C. Yield 72% (MW), 94% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[24] Anal. Calcd. for $C_{14}H_9N_3O_3$: C, 62.92; H, 3.39; N, 15.72; O, 17.96. Found: C, 62.88; H, 3.36, N, 15.74; O, 17.94.

2-(2,2-Dimethylethenyl)-4(3*H*)-quinazoline (entry 10). Yellowish solid, mp 193 – 195 °C. Yield 65% (MW), 92% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[25] Anal. Calcd. for $C_{12}H_{12}N_2O$: C, 71.98; H, 6.04; N, 13.99; O, 7.99. Found: C, 71.95; H, 6.06, N, 14.02; O, 7.96.

2-Cyclopropyl-4(3*H*)-quinazoline (entry 11). Pale yellow solid, mp 232 – 235 °C. Yield 73% (MW), 87% (US). ^{1}H NMR and ^{13}C NMR were in agreement with literature data.[26] Anal. Calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.04; O, 8.59. Found: C, 70.91; H, 5.41, N, 15.02; O, 8.56.

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