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The Novel Green Catalyst: A Three-Component Reaction Using Roselle Salt for the Synthesis of Substituted Chromenos and Xenohormones in Green Chemistry

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Introduction

As the primary building blocks of a wide variety of naturally occurring products, aminochromones are an extremely significant family of organic molecules. They are also useful precursors. cosmetics, pigments, and potentially biodegradable agrochemicals are all products of its synthesis. In addition, fused chromenos are crucial components of pharmacologically active compounds due to their wide range of biological activities, which includes antimicrobial [3, 4], mutagenic [5, 6], antiviral [7, 8], antiproliferative [9, 10], sex pheromonal [10, 11], antitumor [10, 12], and central nervous system (CNS) activities [3, 10]. Due to their ability to produce target products from readily available starting materials in a single reaction step without isolating the intermediates and thereby reducing reaction times, labour cost, and waste production [13], one-pot multicomponent reactions have received considerable attention in synthetic chemistry. Water's availability, low cost, environmental friendliness, neutrality, and status as a naturally occurring solvent have all contributed to its rise in popularity in the past two decades as a solvent for chemical reactions [14, 15]. Due to these factors, water has also been employed for MCRs [16, 17]. Organic synthesis and green chemistry benefit greatly from MCRs in water [16, 17]. In the presence of dangerous organic bases like piperidine and triethylamine, aminochromones may be synthesized by heating a combination of malononitrile, aldehyde, and activated phenol or naphthol's in refluxing DMF or acetonitrile [18, 19]. To the best of our knowledge, the use of clean solvents in conjunction with heterogeneous and reusable catalysts to synthesize these systems is not widely described [13, 25], despite the fact that several synthetic approaches to create these heterocyclic systems have been evaluated [20-36]. We report herein our findings on the utility of Rochelle salt (R. S.) as a green catalyst in the three-component condensations between aromatic aldehydes, active methylene reagents, and action. This work is a continuation of our previous work on the synthesis and biological evaluation of new heterocycles [37-40] and an attempt to explore the efficiency of Rochelle salt (R. S.) as a novel green heterogeneous and reusable

Result and Discussion

The first step in our synthesis included the reaction of aromatic aldehydes 1a-h, malononitrile (2), and resorcinol (3) in a catalytic quantity of refluxing ethanol. 2-Amino-4-aryl-7-hydroxy-4H-chromene-3-carbonitriles 6a-h were synthesized by reaction with Rochelle salt (Scheme 1), table 1.

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Scheme 1: Synthesis of compounds 6-8.

Elemental studies and spectrum data corroborated the structures of the separated compounds 6a-h. Observations of the infrared spectra of the reaction by-products revealed the presence.

functions at 3496-3320 cm1 and acyanoat2200 cm1; OH, and NH2 functions. Two singlets, at = 6.37-6.87 and 9.39-9.61 ppm, were seen in the 1 H NMR spectra, which may be assigned to the amino (NH2) and hydroxyl (OH) groups. In addition, compounds 6a-h formed with high confidence, as shown by 1 H NM. In addition to indications for aromatic protons and other groups, the findings verified the existence of the H-4 proton at =4.57-4.92ppm (see Table 3). In addition, their structures were consistent with the hypothesized structures for compounds 6a-h, as shown by accurate mass spectra and analytical data. Since we are interested in discovering novel ways to synthesis derivatives of the intriguing 1a-h aminochromones, we looked into the useful precursors -naphthol (4) and naphthol (5). The 2-amino-4-aryl-4H-benzo[h] was obtained by reacting a mixture of aromatic aldehydes 1a-h with malononitrile (2) and either naphthol (4) or -naphthol (5) under the same reaction conditions. The 7a-g chromene-3carbonitriles, the 3-amino-1-aryl-1H-benzo[f], and so on. Excellent yields of 8a-h, respectively, of 2chromene-2-carbonitriles. Consistent spectrum data and accurate elemental analysis confirmed the given structures for products (7) and (8). Specifically, see Tables 2 and 3. In contrast, 2amino-4-aryl-7-hydroxy-4H -chromene-3carbonitriles (6a-h) were obtained in high quantities by heating a combination of aromatic alder- hides (1a-h), malononitrile (2), and resorcinol (3) in boiling water containing a catalytic quantity of Rochelle salt. But although -naphthol and

Table 1: Yields and melting points of the synthesized compounds 6–8.



Compound	1.	Tidds	Observed us.p.	Reported m.p.	Reitman
64	23-Dimethosy	15	20		17
db	13-Dimebray	彩	170	_	12
6	3-Beuyloophayl	M	230	-	
61	4-160	86	112-134	18-12	[30,32]
6e	D-6	90	184	164	[30]
6É	н	80	238	214	[32]
4	1.4.5-Trimethoxy	15	230	265	[34]
榆	3-5001	H.	176	168-570	[32]
74	2.3-Dimethoxy	15	260	-	-
ть	2.5 Dimethory	75	240	-	-
7c	1,45-Trimethoxy	80	190	189	[35]
74	10-4	90	235	202	[28]
Te	3-NO ₁	82	236	22	[29]
π	Н	90	205	205	[28]
1	4-Me0	ы	214	265	[35]
84	13-Dimethony	80	240	-	4
8b	2.4-Diracthory	80	36	-	100
k	2.5 Directory	75	266		12
84	3.45-TrimeBuny	括	269	-	÷
he .	3-NO2	81	郎	299	[25]
8	4-560	粒	260	295	[3]
84	H	90	280	278-280	[29]
釉	4-03	11	187	281	[29]

Table 2: Elemental analyses of the newlysynthesized compounds six

Cornered and Company		Elemental analysis			
outiens 1	 MA MIRLEMAN 		C%	H%	8%
60	C ₂ H ₈ N ₂ O ₄	Calc.	66.66	4.97	864
	(33435)	Found	66.41	5.12	834
6	C _a H _a N ₂ O ₄	Calc.	66.66	4.97	8.64
	(324.35)	Found	67.01	5.13	9.01
6c	C_H_N,O,	Calc.	74.58	4.90	736
	(370.48)	Found	76.86	4.75	715
74	C_H_XLO,	Calc.	73.73	5.06	782
	(358.39)	Found	74.11	5.20	8.67
ъ	C ₂ H ₂ N ₂ O ₅	Calc.	73,73	5.06	732
	(358.39)	Found	74,02	5.38	738
82	C ₂ H ₂ N ₂ O ₅	Calc.	73.73	5.06	782
	(358.39)	Found	74.8	5.74	8.21
5	C ₂ :H ₀ ,N ₂ O ₁	Calc.	73,73	5.06	7.82
	(358.39)	Found	73,63	4.83	8.19
k	C ₂ H ₂ N ₂ O ₅	Calc.	73.73	5.06	782
	(358.39)	Found	73.52	5.34	763
si	C ₂ H ₂ N ₂ O ₄	Calc.	71 <u>0</u>	5.89	721
	(388.42)	Found	7134	5.40	750

Even after prolonged heating, a-naphthol performed the aforementioned one-pot, threecomponent reactions in boiling water. An ethanol and water combination were the norm as a good yields of the intended products 6a-h, 7a-g, and 8a-h were obtained from the preceding reactions involving the three phenols in the presence of the solvent.

Every compound had the same physical and spectral properties as all the others that have been documented in the literature.

Table 3: Spectral data of the newly synthesizedcompounds 6–8.

Compand	IR(m ⁻¹)	NS	¹ Η NMB. (DMSO-4], (δ ppm)
輪	349-3327 (OH and NEL), 299 (CN)	334(M')	3.65 (s, 32), 00E4, 3.37 (s, 32), 00E5, 4.89 (s, 12), 12-40, 6.35 (s, 22), 345, 6.65-6.34 (n, 62), 347, 368 (br.s, 12), 005.
พี	3404-3825 (OH and NH ₂), 220 (ON)	334(M*)	348 (s. 111, OCH.), 373 (s. 311, OCH.), 442 (s. 111, 11-4), 637 (s. 211, MEL), 657-675 (m. 611, ArH), 933 (br.s. 111, OH)
6c	369-300 (OH and NH ₂), 205 (CN)	370 (M [*])	457 (x1H, H-4), 514 (x, 2H, -CH ₂ -), 637-682 (m, 5H, ArH), 687 (x, 2H, NH ₂), 722-737 (m, 3H, ArH), 744-744 (m, 4H, ArH), 839 (m x, 1H, OH),
'n	$\rm B87, \rm B87, \rm B80 (\rm NH_2), \rm 290 (\rm CN)$	358(M*)	3.64(x)组,0CE),3.79(x)组,0CH),5.14(x)组,组组4,669(x)组 3.64(x)4-755(m,941,644)
ъ	BRC, 335 (NH ₂), 285 (CN)	358(M*)	3.71(5.11,0CE),130(6.31,0CE),454(5.11,E-4),672(6.31, NB),734-755(m,91,445).
ŝa	3460, 3340 (NH ₂), 2200 (CN)	358(M')	315年1月00日,14月1日第100日,142年1月4月666年1日 31日,721-735年1月1日
Б	3465, 3300 (NH ₂), 2200 (CN)	358(M*)	342 (s, 38, 0CH,), 391 (s, 3H, 0CH,), 454 (s, H, H-4), 672 (s, 2H, 343), 724-735 (n, 9H, 34H)
k	3450, 3320 (NH ₂), 247 (CN)	358 (M*)	3.7% 第,0CH,1.332(6,1H,0CH),455(6,H,H-4),669(6,H, 365),728-725(点,死,34H)
Ы	3465, 330 (NH ₂), 291 (CN)	388(M')	3.70 (s, EL, OCH, J. 381 (s, EL, OCH, J. 389 (s, 3H, OCH, J. 450 (s, EL, H-4), 6.64 (s, 2H, NH, J. 721-378 (m, 8H, ArH).

Conclusions

New 2-amino chromenos can be synthesized in a way that is both environmentally friendly and productive. by using Rochelle salt as a unique green catalyst, two compounds of anticipated biological importance, benzo[h]chromenos and benzo[f]chromones, were synthesized. We believe this to be the first time Rochelle salt has been used as a catalyst in one-pot three-component reactions due to its efficiency, environmental friendliness, and low cost.

Experimental

General. The melting points listed here are the raw results of Gal- encamp instrument measurements. IR spectroscopy was captured using a KBr disk and a Shimadzu FT-IR 8101 PC spectrophotometer. Chemical shifts () are given in parts per million, and 1 H NMR spectra were acquired at 300 MHz on a Bruker 300 spectrometer using DMSO-d6 and CDC13 as solvents and TMS as an internal standard. The mass spectra were obtained using a GCMS-QP1000 EX (EI, 70 eV) instrument. Thinlaver chromatography (TLC) analysis was conducted on 0.25-millimeter-thick Merck silica gel sixty plates stained with F-254 indicator. UV light enabled the process of visualisation. Chromatography solvents were used as supplied and were of reagent grade quality. The Data Unit for Microanalysis at Cairo University conducted the analyses. The solid by-products were separated by filtering, dried, and recrystallized from EtOH at room temperature to yield chromones 6a-h. Technique (B). Rochelle salt (0.3 g) was added to a



solution of are- Matic aldehydes (1a-h) (5 mmol), malononitrile (2) (5 mmol), and resorcinol (3) (5 mmol) in H2 O (10 mL). Chromenos 6a-h were obtained by further processing the reaction mixture in the manner outlined above. Synthesis of 2-Amino-4-aryl-4H- benzo[h]: A General Protocol7ag Chromene-3-Carbonitriles and 3-Amino-1-aryl-1H-Benzo[f]The Chromenes-8a-h 2Carbonitriles.Rochelle salt (0.3 g) was added to a mixture of aromatic aldehydes (1a-h), malononitrile (2), and 1-naphthol (4) (or 2-naphthol (5)) in ethanol or an ethanol/water combination (1: 1) (10 mL) with molar ratios of 5 mmol to 2 mmol. For around four to eight hours, we let the reaction mixture simmer at a low simmer. The solid byproducts 7a-g and 8a-h were recovered after cooling to room temperature by filtering, dried, and recrystallized from EtOH.

Conflict of Interests

The author confirms that he or she has no competing interests in seeing this research published.

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