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Fast highly efficient 'on-solvent' non-catalytic cascade transformation of benz-aldehydes and 4-hydroxycoumarin into bis(4-hydroxycoumarinyl)arylmethanes

Michail N. Elinson,* Anatoly N. Vereshchagin, and Olga O. Sokolova

Department of Organic Chemistry, N. D. Zelinsky Institute of Organic Chemistry, Leninsky prospect 47, 119991 Moscow, Russia
E-mail: elinson@ioc.ac.ru

Dedicated to Prof. Oleg A. Rakitin on the occasion of his 65th birthday

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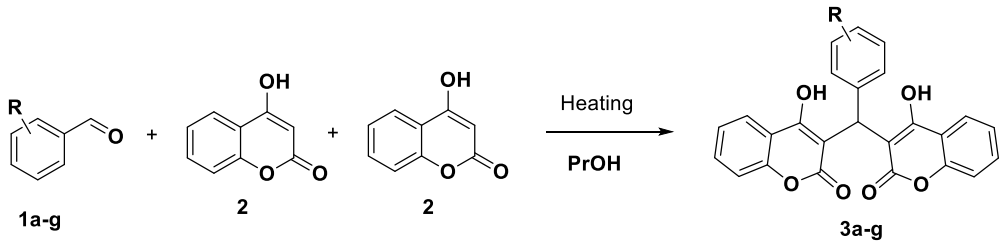
Abstract

Non-catalytic cascade reaction of benzaldehydes and two equivalents of 4-hydroxycoumarin initiated by reflux in propanol results in the fast (15 min) and efficient formation of substituted tetrahydro-1*H*-xanthen-1-ones in 93–98% yields. The developed fast cascade approach to the substituted bis(4-hydroxycoumarinyl)arylmethanes, which are known as medicinally relevant substances with anti-HIV, antibiotic, anti-inflammatory and anti-cancer activity, is beneficial from the viewpoint of diversity-oriented large-scale processes and represents fast, efficient and environmentally benign synthetic concept for cascade reactions strategy.



a R = H, b R = 4-Me, c R = 2-OMe,
d R = 4-*t*-Bu, e R = 4-Cl, f R = 4-F
g R = 3-Br

Keywords: Non-catalytic, carbanions, 4-hydroxycoumarin, bis(4-hydroxycoumarinyl)aryl-methanes, green chemistry

Introduction

Cascade reactions are known as powerful method to construct molecular complexity from readily available starting materials by combining two or more reactions into a single transformation.[1,2] Cascade reactions forming a number of bonds by one operation are useful for the creation of polycyclic and spirocyclic compounds.[3] Thus, cascade reactions are of increasing importance in modern organic chemistry. This is not only due to the need for the more efficient and less labour-intense methodologies for the synthesis of pharmaceuticals and other fine chemicals, but also because of the increasing importance of the environmental considerations.[4,5]

Coumarins or benzopyran-2-ones, are one of the most known oxygen heterocyclic compounds which are efficiently studied from their discovery up to our days.[6] The great interest to these compounds is due to their known anti-cancer,[7,8] anti-inflammatory,[9] antihyperlipidemic[10] anticholinesterase,[11] antinociceptive,[12] antidiabetic and antidepressant[13] activities.

4-Hydroxycoumarins are important class of biologically active substances in nature and in medicine. They exhibit sufficient anticoagulant activity and among them, there are some drugs – Warfarin and Acenocoumarol. Many of them display important pharmacological effects, as anti-inflammatory[14], anti-cancer,[15] anti-HIV and antiviral[16] agents.

Dicoumarol (a coumarin anticoagulant, 3,3'-methylenebis[4-hydroxycoumarin]) is a competitive NADH quinone oxidoreductase (NQO1) inhibitor, and used as an anticoagulant by interfering with the metabolism of vitamin K. Dicoumarol is known as microtubule stabilizing natural product that is synergistic with Taxol.[17] Dicoumarol also potentiates cisplatin-induced apoptosis urogenital cancer cell lines.[18] Dicoumarol and its derivatives display wide range of pharmacological activity such as anti-HIV,[19,20] antibiotic,[21] antitumor and anti-inflammatory.[22]

Dicoumarols are generally synthesized by cascade reaction of two equivalents of 4-hydroxycoumarin and different aldehydes. In the recent years, several methods have been reported to accomplish this reaction. In most of them, different catalysts are used, such as molecular iodine,[23] DBU,[24] piperidine,[25] $MnCl_2$,[26] propane-1,2,3-triyltris(hydrogen sulfate),[27] tetrabutylammonium bromide (TBAB),[28] tetrabutylammonium hexatungstate,[29] dodecylbenzene sulfonic acid (DBSA),[30] silica chloride nanoparticles (nano SiO_2Cl).[31] Refluxing for long time (5-6 hours) in ethanol[32] or acetic acid[33] are also known.

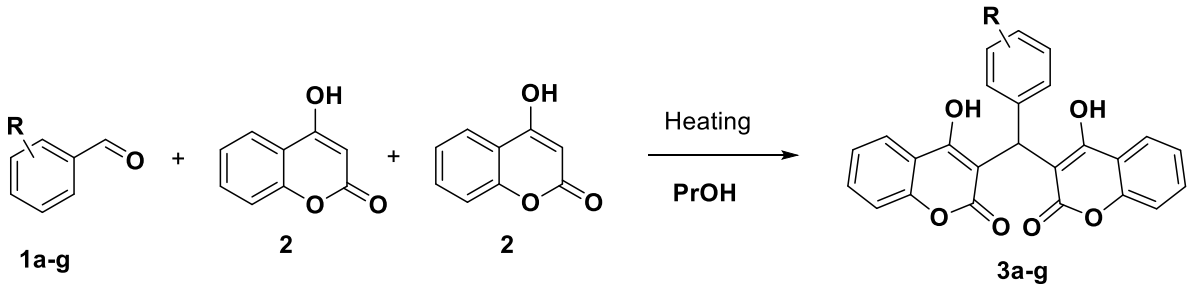
Although all this procedures for the synthesis of corresponding dicoumarols have their merits, but all of them suffer from some drawbacks, such as unsufficient yields, prolonged reaction times, the use of costly reagents or catalysts. The recovery of the catalyst and the procedure of isolation pure dicoumarols may also be complicated in many cases.

Recently we have accomplished some non catalytic cascade and multicomponent reactions of carbonyl compounds and C-H acids.[34-38] Considering our results on the non-catalytic multicomponent and cascade transformation of C-H acids and carbonylcompounds[34-38] as well as the certain biomedical application of bis(4-hydroxycoumarinyl)arylmethanes mentioned above, we were prompted to design a convenient fast and facile non-catalytic methodology for the fast efficient cascade synthesis of substituted bis(4-hydroxycoumarinyl)arylmethanes based on cascade reaction of of benzaldehydes and 4-hydroxycoumarin.

Results and Discussion

As it follows from introduction, we were interested in designing a fast convenient and facile non-catalytic methodology for the efficient synthesis of functionalized bis(4-hydroxycoumarinyl)arylmethane system based

on multicomponent reaction of benzaldehydes **1a-g**, and 4-hydroxycoumarine (**2**) (Scheme 1, Tables 1 and 2).



a R = H, b R = 4-Me, c R = 2-OMe,

d R = 4-*t*-Bu, e R = 4-Cl, f R = 4-F

g R = 3-Br

Scheme 1. Cascade transformation of benzaldehydes **1a-g** and 4-hydroxycoumarin (**2**) into 3,3'-(arylmethylene)bis(4-hydroxy-2*H*-chromen-2-ones) (**3a-g**).

On the first step of this investigation the transformation of benzalaldehyde **1a** and two molecules of 4-hydroxycoumarine (**2**) was studied (Table 1).

Table 1. Cascade transformation of benzaldehyde (**1a**) and 4-hydroxycoumarin (**2**) into 3,3'-(phenyl-methylene)bis(4-hydroxy-2*H*-chromen-2-one) (**3a**)[a]

Entry	Solvent (mL)	Catalyst (mol%)	T (°C)	Time (min)	Yield[b] (%)
1	EtOH, 10	NaOAc, 10%	78	30	76
2	EtOH, 10	KF, 10%	78	30	74
3	EtOH, 10	—	78	30	75
4	EtOH, 10	—	78	15	70
5	*n*-PrOH, 10	—	97	30	85
6	*n*-PrOH, 5	—	97	30	88
7	*n*-PrOH, 3	—	97	30	93
8	*n*-PrOH, 1	—	97	30	96
9	*n*-PrOH, 1	—	97	20	95
10	*n*-PrOH, 1	—	97	15	95
11	*n*-PrOH, 1	—	97	10	93
12	—	—	95-100	30	85

[a]Reaction conditions: 4-hydroxycoumarin (1.62 g, 10 mmol); benzaldehyde (0.53 g, 5 mmol).

[b]Isolated yield.

In ethanol as a solvent under reflux (78 °C) in the presence of NaOAc or KF as catalyst in 30 min. reaction time 3,3'-(phenylmethylene)bis(4-hydroxy-2*H*-chromen-2-one) (**3a**) was obtained in 76 and 74% yield (entries 1,2; Table 1).

The most interesting was the fact that just the same yield (75%) was obtained in ethanol without any catalyst (entry 3, Table 1). Somewhat lower yields 70% were found when reaction time was shortened to 15 min.

The yield of 3,3'-(phenyl-methylene)bis(4-hydroxy-2*H*-chromen-2-one) (**3a**) was increased to 85%, when reaction was carried out in boiling propanol (97° C) without any catalyst (entry 5, Table 1).

In the last years the concept of 'on-water' and 'on-solvent' reactions with using minimum quantities of the solvents to carry out reactions in suspensions or emulsions has been developed.[39-43] Thus, further minimization of the quantity of solvent and reaction time have been investigated showing improved yields (entries 5-8, Table 1) while no-solvent conditions result in some yield's decrease (entry 12, Table 1).

Under optimal non-catalytic conditions (1 mL of PrOH, 97 °C, 15 min) 3,3'-(phenyl-methylene)bis(4-hydroxy-2*H*-chromen-2-one) (**3a**) was obtained in 95% yield.

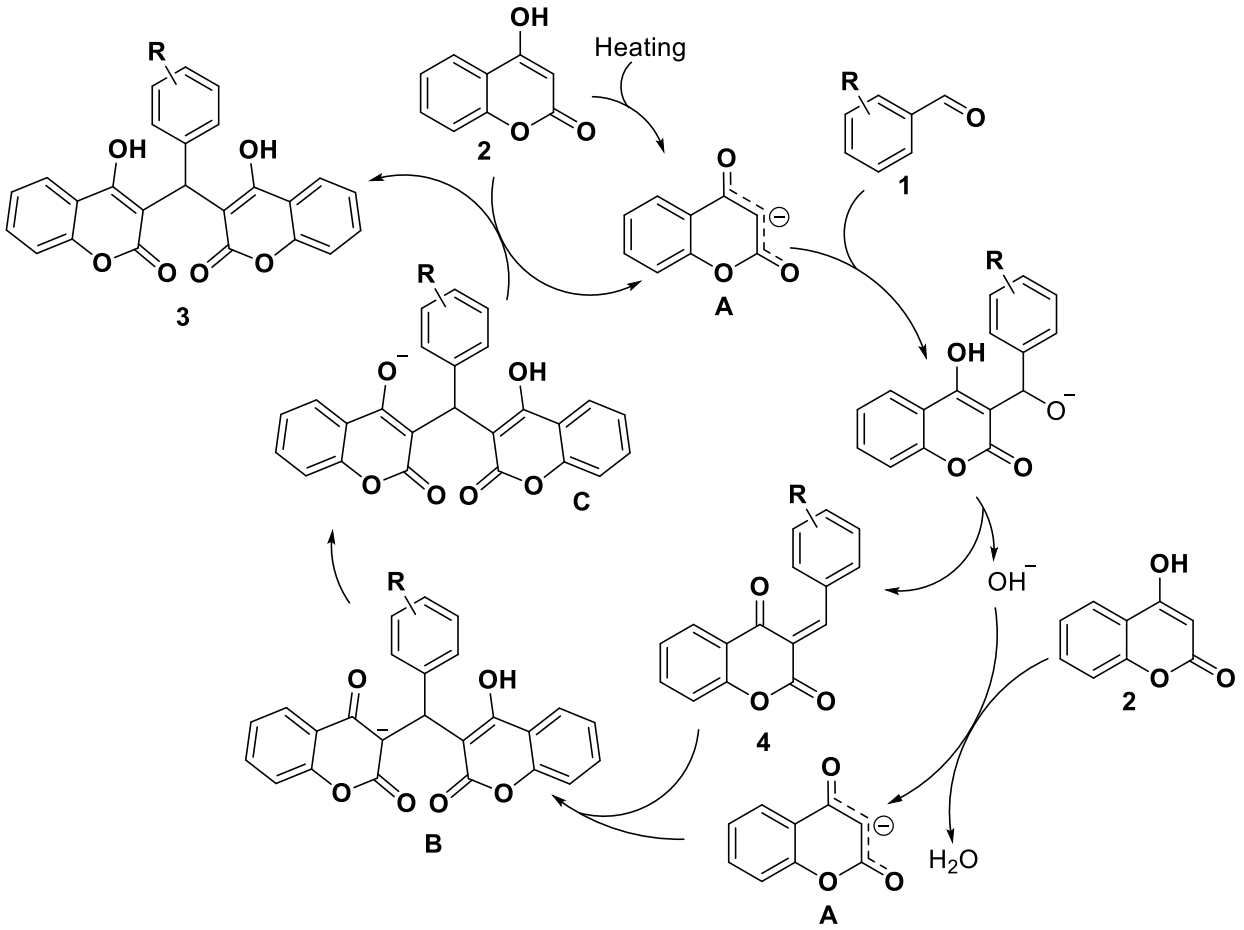
Under these optimal conditions 3,3'-(arylmethylene)bis(4-hydroxy-2*H*-chromen-2-ones) **3a-g** were obtained in 93-98% yield (Table 2).

Table 2. Synthesis of biscoumarin derivatives **3a-g**[a]

Entry	R	Yield[a] (%)
1	H	95
2	4-Me	98
3	2-OMe	96
4	4-*t*Bu	93
5	4-Cl	97
6	4-F	95
7	3-Br	96

[a]Reaction conditions: 4-hydroxycoumarin (1.62 g, 10 mmol); substituted benzaldehyde (5 mmol); *n*-PrOH, 1 mL; 97 °C, 15 min.
[b]Isolated yield.

With the above results taken into consideration and the mechanistic data on non-catalytic 'domino' transformations[36-38] the following mechanism for the non-catalytic cascade transformation of benzaldehydes **1** and 4-hydroxycoumarin (**2**) into 3,3'-(arylmethylene)bis(4-hydroxy-2*H*-chromen-2-ones) **3** was suggested. The initiation step of the catalytic cycle is the thermal deprotonation of a molecule of 4-hydroxycoumarin **2** with the 4-hydroxycoumarin anion **A** formation (Scheme 2).



Scheme 2. Cascade transformation of benzaldehydes **1** and 4-hydroxycoumarin (**2**) into 3,3'-(arylmethylene)bis(4-hydroxy-2*H*-chromen-2-ones) **3**.

Knoevenagel condensation of the anion **A** with benzaldehydes **1** leads to formation of Knoevenagel adduct **4** with the elimination of a hydroxide anion.[44] The subsequent hydroxide-promoted Michael addition of 4-hydroxycoumarin (**2**) to electron-deficient Knoevenagel adduct **4** results in subsequent anions **B** and **C** formation. Protonation of anion **C** with the next molecule of 4-hydroxycoumarin **2** leads to the corresponding 3,3'-(arylmethylene)bis(4-hydroxy-2*H*-chromen-2-one) **3** formation with the regeneration of anion **A** at the last step of the catalytic cycle (Scheme 2).

Conclusions

The very simple and fast (15 min.) non-catalytic procedure can produce an efficient and selective transformation of benzaldehyde, and 4-hydroxycoumarin into substituted 3,3'-(arylmethylene)bis(4-hydroxy-2*H*-chromen-2-ones) in excellent 93-98% yields. This new non-catalytic cascade process opens an efficient and convenient way to substituted 3,3'-(arylmethylene)bis(4-hydroxy-2*H*-chromen-2-ones), the pharmacologically active substances with known anti-HIV, antibiotic, anti-inflammatory, anti-cancer activity and promising compounds for different biomedical applications. This non-catalytic cascade procedure utilizes simple equipment; it is easily carried out and is valuable from the viewpoint of environmentally benign diversity-oriented large-scale processes.

Experimental Section

General. All melting points were measured with a Gallenkamp melting-point apparatus and are uncorrected. ^{1}H spectra were recorded in $CDCl_3$ with a Bruker Avance II 300 spectrometer at ambient temperature. Chemical shift values are relative to Me_4Si. All chemicals used in this study were commercially available.

General procedure. A mixture of 4-hydroxycoumarin (1.62 g, 10 mmol) and benzaldehyde (5 mmol) in 1 mL of *n*-PrOH was heated under stirring at 97 °C for 15 min. Then the precipitated product was filtered off, rinsed with an ice-cold ethanol (1 mL) and dried under reduced pressure.

3,3'-(Phenylmethylene)bis(4-hydroxy-2*H*-chromen-2-one) (3a). White solid; 1.98 g (95%); mp 230-231 ºC (Lit. mp[45] 228-230 ºC); δ_H (300 MHz, $CDCl_3$): δ 6.13 (s, 1H, CH), 7.10–8.17 (m, 13H, Ar), 11.33 (br s, 1H, OH), 11.55 (br s, 1H, OH).

3,3'-((2-Methoxyphenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3b). White solid; 2.17 g (98%); mp 225-226 ºC (Lit. mp[46] 225-226 °C); δ_H (300 MHz, $CDCl_3$): δ 3.60 (s, 3H, OCH_3), 6.11 (s, 1H, CH), 6.80–8.09 (m, 12H, Ar), 11.23 (br s, 2H, 2×OH).

3,3'-(*p*-Tolylmethylene)bis(4-hydroxy-2*H*-chromen-2-one) (3c). White solid; 2.06 g (96%); mp 267-268 ºC (Lit. mp[45] 266-268 ºC); δ_H (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 6.09 (s, 1H, CH), 7.05–8.13 (m, 12H, Ar), 11.31 (br s, 1H, OH), 11.53 (br s, 1H, OH).

3,3'-((4-(*tert*-Butyl)phenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3d). White solid; 2.18 g (93%); mp 250-251 ºC (Lit. mp[47] 247-248 °C); δ_H (300 MHz, $CDCl_3$): δ 1.33 (s, 9H, 3×CH_3), 6.09 (s, 1H, CH), 7.11–8.12 (m, 12H, Ar), 11.28 (br s, 1H, OH), 11.51 (br s, 1H, OH).

3,3'-((4-Chlorophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3e). White solid; 2.17 g (97%); mp 260-261 ºC (Lit. mp[48] 256-258 °C); δ_H (300 MHz, $CDCl_3$): δ 6.06 (s, 1H, CH), 7.11–8.15 (m, 12H, Ar), 11.33 (br s, 1H, OH), 11.55 (br s, 1H, OH).

3,3'-((4-Fluorophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3f). White solid; 2.04 g (95%); mp 213-214 ºC (Lit. mp[48] 211-212 °C); δ_H (300 MHz, $CDCl_3$): δ 6.07 (s, 1H, CH), 6.95–8.16 (m, 12H, Ar), 11.33 (br s, 1H, OH), 11.56 (br s, 1H, OH).

3,3'-((3-Bromophenyl)methylene)bis(4-hydroxy-2*H*-chromen-2-one) (3g). White solid; 2.36 g (96%); mp 275-276 ºC (Lit. mp[45] 280-282 °C); δ_H (300 MHz, $CDCl_3$): δ 6.09 (s, 1H, CH), 7.08–8.13 (m, 12H, Ar), 11.31 (br s, 1H, OH), 11.53 (br s, 1H, OH).

Acknowledgements

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