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Unique versatility of Amberlyst 15. An acid and solvent-free paradigm towards synthesis of bis(heterocyclyl)methane derivatives

Kamaljit Singh*, Shivali Sharma, Amit Sharma

Organic Synthesis Laboratory, Department of Applied Chemical Sciences & Technology, Guru Nanak Dev University, Amritsar 143 005, India

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ABSTRACT

Bis(heterocyclyl)methanes, key intermediates for a variety of chemical, biochemical and material science relevant targets, have been obtained in a synthetically useful manner using Amberlyst 15 ion-exchange resin. This method promises versatility, cost-effectiveness, and efficiency.

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1. Introduction

Bis(heterocyclyl)methanes constitute highly valuable building blocks in the context of natural and unnatural porphyrinoids [1,2], and are of immense importance biologically, industrially and indeed in material science applications [3–13]. As a consequence, bis(heterocyclyl)methane derivatives are important synthetic targets.

Condensation of heteroaryl species with carbonyl substrates, typically aldehydes, is a challenging task and owing to high reactivity and vulnerability of the latter, especially aliphatic counterparts, towards both alkali as well as acid reagents, side reactions ensue, which furnishes the required product in lower yield. Two types of synthetic methods have been used for the synthesis of bis(heterocyclyl)methane derivatives. The widely used approach for the synthesis of bis(pyrrol-2yl)methane derivatives, relies on a one-pot condensation of pyrrole and desired aldehydes in acidified solvents. Essentially, in these methods, the condensation reaction completes only when a large excess of the expensive pyrrole is employed. Likewise, in case of analogous condensation reactions of thiophene, thiophene: aldehyde ratios often exceed 37:1, to drive the reaction to completion and to suppress the formation of unwanted linear/cyclic oligomers and/or by-products of carbonyl counterparts. Use of metal cation-exchanged Montmorillonite [14a] and clay (K10) [14b] has also been implemented successfully, for such condensation reactions with or without a solvent. We recently reported synthesis of *meso*-elaborated bis(pyrrol-2yl)methane [15], bis(thien-2yl)methane [16] as well as bis(furan-2yl)methane [17] derivatives, employing a highly regioselective, low temperature *meso*-lithiation of appropriate *meso*-unsubstituted bis(heterocyclyl)methane, followed by reaction with an electrophile. However, in the context of environmental and industrial concerns, use of low temperature reaction conditions and/or organolithium reagents limit the practical applicability of the latter approach. Amberlyst 15 ion exchange resin has been implemented in a number of condensation reactions [18–20] and other organic transformations [21]. However, in many events, either a higher molar ratio of reactants [22] was required which eventually led to the formation of side products [23] or the condensation required longer reaction time [24] and/or a solvent [25] medium for reaction. We have now found that using Amberlyst 15 ion exchange resin pyrroles, furan, thiophene and indole condense with a number of aldehydes (Scheme 1), to furnish the title derivatives, in a synthetically useful manner (without solvent, near stoichiometric ratios) avoiding the limitations cited above.

2. Results and discussion

Mixing Amberlyst 15 ion exchange resin (0.02 g/mmol of aldehyde) with thiophene (3.0 mmol) and benzaldehyde **7a** (1.0 mmol) in the absence of solvent, results in mild exothermic reaction (2 °C increase in temperature). The reaction completed upon heating at 80 °C, for 25 min resulting in the formation of phenyl-di(thien-2yl)methane **8a** in 78% yield (Table 1). The requirement of 1.0 molar

* Corresponding author. Tel.: +91 1832258802 09; fax: +91 1832258820.
E-mail address: kamaljit19in@yahoo.co.in (K. Singh).

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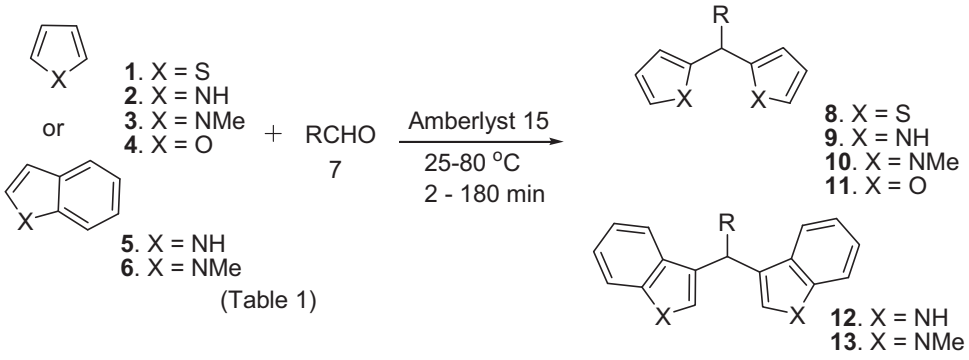


Scheme 1. Condensation of electron rich heterocycles with aldehydes (Table 1).

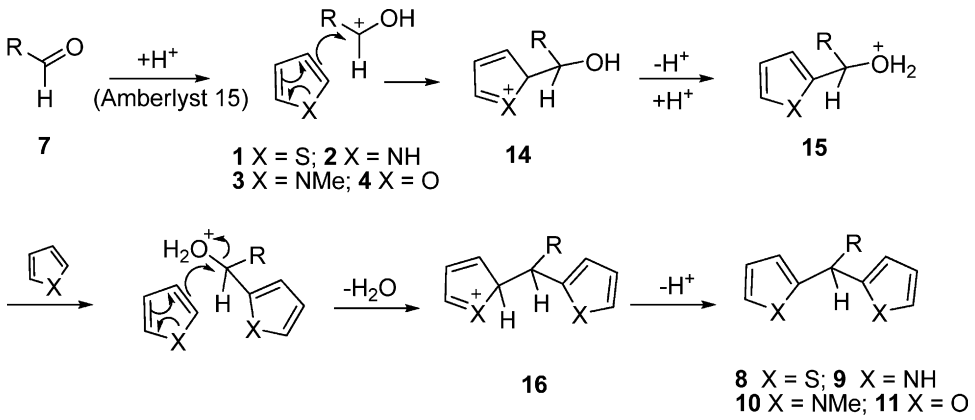
excess of thiophene (3.0 mmol) was offset by the rapid completion of the reaction, good yield of **8a** and absence of any by-product in the reaction. The catalyst could be recycled for at least five batches without significant loss in its activity, an observation which is merited in any industrial process. Using Amberlyst 15, the generality of the condensation reaction of thiophene with several aromatic aldehydes **7b–t**, substituted with electron donating/withdrawing groups on the phenyl ring as well as varying steric hindrance, was checked. The corresponding products **8b–t** were isolated in 60–85% yields (Table 1). Further, reaction of aldehyde **8t** with thiophene, under similar set of conditions furnished, 1,4-bis(dithiophen-2yl-methyl)benzene **8u** in 65% yield.From these reactions, it is apparent that the *meso*-substituted bis(thien-2yl)methane derivatives **8** were formed in good yield and without any side product, besides the protocol was found to be tolerable to a variety of substituents such as 4-Me, 4-Cl, 4-Br, 4-CN, 4-/3-OH, 2-/3-/4-NO_2, 2-CF_3, 3,4-/2,4-/2,5-di-MeO, 3,4,5-tri-MeO, and 2,4,6-tri-Me on the aldehyde component. Irrespective of the electronic nature of the substituent and their position on the aryl group, the reactions aided by Amberlyst 15 showed high reactivity as all the reactions got completed in favourably short time (20–30 min).

Bis(pyrrol-2yl)methane derivatives are important intermediates for the preparation of synthetic porphyrins [1] and related compounds (dipyrrins, calix[n]pyrroles, chlorins, corroles). Unlike naturally occurring porphyrins, which are substituted at the β-positions and unsubstituted at the *meso*-positions, synthetic porphyrins are invariably substituted at the *meso*-positions and lack substituents at the β-position. Bis(pyrrol-2yl)methanes are also frequently used as precursors to dipyrromethenes, which are important ligands in the design of macromolecular structures. Difluoroboron complexes of dipyrromethenes, (BODIPY) derivatives are used as fluorescent dyes for biological samples [26]. Access [27] to such building blocks has thus far relied mainly on one-pot condensations of pyrrole and the desired aldehydes in acidified

Table 1
Amberlyst 15 catalyzed condensation of heterocycles **1–6** with aldehydes **7**.

RCHO	Products **8–13** (% yield)[a]					
	Thiophene[b]	Pyrrole[c]	N-Me Pyrrole [c]	Furan[d]	Indole[e]	N-Me indole[e]
7 R	**1**	**2**	**3**	**4**	**5**	**6**
7a Ph	**8a** (78)	**9a** (60)	**10a** (75)	**11a** (65)	**12a** (98)	**13a** (95)
7b 4-MeO-C_6H_4	**8b** (80)	**9b** (65)	**10b** (70)	**11b** (62)		
7c 4-Me-C_6H_4	**8c** (75)		**10c** (72)	**11c** (60)	**12b** (65)	
7d 4-Cl-C_6H_4	**8d** (78)	**9c** (75)	**10d** (75)	**11d** (70)		
7e 4-Br-C_6H_4	**8e** (82)	**9d** (75)	**10e** (70)	**11e** (74)	**12c** (68)	
7f 4-CN-C_6H_4	**8f** (85)	**9e** (80)		**11f** (65)	**12d** (75)	
7g 4-OH-C_6H_4	**8g** (74)	**9f** (75)	**10f** (74)			
7h 3-OH-C_6H_4	**8h** (76)			**11g** (64)		
7i 4-NO_2-C_6H_4	**8i** (82)		**10g** (72)		**12e** (80)	
7j 3-NO_2-C_6H_4	**8j** (80)	**9g** (80)	**10h** (75)	**11h** (70)		
7k 2-NO_2-C_6H_4	**8k** (75)		**10i** (75)			
7l 2-CF_3-C_6H_4v	**8l** (72)					
7m 2-$C_{10}H_7$	**8m** (72)	**9h** (80)	**10j** (82)	**11i** (80)	**12f** (82)	
7n 3,4-$(MeO)_2$-C_6H_3	**8n** (80)		**10k** (70)			
7o 3,4,5-$(MeO)_3$-C_6H_2	**8o** (78)	**9i** (82)	**10l** (75)	**11j** (75)	**12g** (80)	
7p 2,4-$(MeO)_2$-C_6H_3	**8p** (74)			**11k** (65)		
7q 2,5-$(MeO)_2$-C_6H_3	**8q** (72)	**9j** (74)			**12h** (85)	
7r 2,4,6-$(Me)_3$-C_6H_2	**8r** (60)					
7s thien-2yl	**8s** (62)	**9k** (75)	**10m** (68)	**11l** (65)		
7t OHC-*p*-C_6H_4-	**8t** (60)	**9l** (74)	**10n** (65)	**11m** (64)	**12i** (94)	**13b** (92)
7u pyrrol-2yl		**9m** (75)				
7v furan-2yl		**9n** (76)	**10o** (78)			**13c** (96)
7w N-Me pyrrol-2yl			**10p** (78)			
7x indole-3yl					**12j** (94)	
7y N-Me-indole-3yl						**13d** (96)
8t 2,2′-bis(thien-2yl) CHC_6H_4-	**8u** (65)	**9o** (75)	**10q** (78)		**12k** (82)	**13e** (85)

[a] Isolated yields (For complete experimental details and spectral data see Supporting information).
[b] **1** (3.0 mmol), **7** (1.0 mmol), Amberlyst 15 (0.02 g), 80 °C, 20–30 min.
[c] **2**/**3** (3.0 mmol), **7** (1.0 mmol), Amberlyst 15 (0.02 g), 80 °C, 2–3 min.
[d] **4** (5.0 mmol), **7** (1.0 mmol), Amberlyst 15 (0.02 g), 25 °C, 3 h.
[e] **5**/**6** (3.0 mmol), **7** (1.0 mmol), Amberlyst 15 (0.02 g), 80 °C, 15 min.



Scheme 2. Plausible mechanism of formation of bis(heterocyclyl)methane derivatives **8**–**11**.

solvents: $BF_3.OEt_2/CH_2Cl_2$, acetic acid/DMF or THF, $SnCl_4/CH_2Cl_2$, *p*-toluenesulfonic acid/MeOH or toluene, or aqueous HCl/THF. In most of these syntheses a large pyrrole:aldehyde ratio (up to 400:1) is employed to drive the reaction to completion and to suppress reactions leading to unwanted linear/cyclic oligomers. Further, the non-availability of many functionalized aldehydes, the failure of aliphatic aldehydes to react and their propensity to show side reactions limit the scope of this route. The indirect synthesis through the use of perhydro 1,3-heterocycles [28], was also attended by the formation of tripyrranes. To extend the synthetic utility of the current protocol, and to develop a direct route to *meso*-substituted bis(pyrrol-2yl)methanes, we performed condensation reactions of pyrrole with aldehydes, using Amberlyst 15 ion exchange resin as catalyst. Thus reaction of **2** with benzaldehyde **7a** in the presence of Amberlyst 15 (0.02 g/mmol of **7a**), in solvent-free reaction conditions, furnished phenyl-di(pyrrol-2yl)methane **9a** in 60% yield. The reaction completed fairly rapidly and furnished the product during 2–3 min. Similar reactions of **2** with a selected number of aldehydes **7b, 7d**–**g**, **7j**, **7m**, **7o**, **7q**, **7s**–**v**, furnished corresponding products (Table 1), in yields ranging from 65–80%. Using **8t**, as carbonyl component, and pyrrole, corresponding product 2,2′-((4-(dithiophen-2-ylmethyl)phenyl)methylene)bis(1*H*-pyrrole) **9o** was obtained in 75% yield. In comparison to the reactions of thiophene, reactions of pyrrole with aldehydes **7** were facile and completed within 2–3 min and afforded the corresponding products in good yield (Table 1). Likewise, reactions of N-methyl pyrrole were conducted with **7** and **8t**, using Amberlyst 15 as promoter. Corresponding products **10** were obtained in both high yield as well as efficiency.

Meso-elaborated bis(furan-2-yl)methanes exhibit interesting chemistry and biology [29]. These are also important intermediates for the synthesis of dicationic tetraoxaporphyrins [2a] calix[n]furans [3], etc. The available routes for the synthesis of bis(furan-2-yl)methane derivatives generally rely on the acid-catalyzed condensation of furan with aldehydes [30b] or furfuryl alcohol [30c], which often result in complex product mixtures owing to the domination of oligomeric by-products. Alternatively, condensation of (2-furyl)lithium with furfuraldehyde, followed by $NaBH_4$ reduction also furnishes bis(furan-2-yl)methanes [3]. In contradistinction to the condensation reactions of **1**–**3**, the reactions of furan **4** with aldehydes **7** required 5.0 equiv. for completion. To check the volatility of furan (b.p. 32 °C) the reactions with aldehydes were performed at 25 °C and invariably required longer time (3 h) for completion, however, furnished corresponding products **11** in satisfactory yields (Table 1).

Bis(indolyl)methanes **12**/**13** constitute structural feature of a number of naturally occurring compounds [31] and display diverse pharmacological activities [13] in addition to their application [11] in material science, agrochemicals and dyes. To access these targets, condensation of indole and aldehydes through the use of protic [32a] and Lewis acids has been usually employed [32b,32c,33]. However, many such routes suffer from the limitation of lower yields of the products, requirement of large or at least stoichiometric amount of a catalyst, intricate catalyst preparation in some cases, longer reaction times and lower yields of the products. Previously, use of ion exchanger/silica supported sodium hydrogen sulphate has been described to furnish bis- and tris(indolyl)methane derivatives during 2.5–3 h when the reactions of indole and aldehydes were conducted in methylene chloride [34]. To further extend the synthetic scope of the solvent-free Amberlyst 15 catalyzed protocol, we have performed reactions of indole **5** and N-methyl indole **6** with **7**. The reactions were very facile, completing within 15 min after mixing the reactants and furnished corresponding products **12** and **13**, in near quantitative yield (Table 1), without any side products.

The formation of the products **8**–**11** can be visualized through the mechanism proposed in (Scheme 2). Thus, initial reaction of an appropriate electron rich species **1**–**4** with carbonyl substrate, activated through protonation by Amberlyst 15, leads to the adduct **15** obtained from initially formed **14**. Similar nucleophilic C-2 attack by **1**–**4** result in the adduct **16** which after deprotonation furnishes products **8**–**11**. Similarly, reactions at β-positions of enamines **5** or **6** with **7** would lead to the formation of corresponding bis(indolyl)methane **12**/**13** derivatives.

It is worth noting that, using **7s**, **7u**–**y** as carbonyl substrates, condensations with relevant electron rich heterocycles **1**–**6** was very facile and the corresponding tri(heterocyclyl)methane derivatives are useful agents from synthetic, medicinal as well as industrial point of view [35]. Apart from their use as protective agents; they possess coloristic properties as well as exhibit antitumor [36] and antioxidant activities [37]. Further, formation of only mono-condensed products in the condensation of terephthaldehyde **7t** with **1**–**4** is a synthetically useful operation since the subsequent condensation of second carbonyl opens a route for the synthesis of unsymmetrically substituted systems, which are otherwise formed with difficulty. To achieve this objective, reaction of **8t** were performed with **1**–**3**, **5**, **6** and the corresponding products **8u**, **9o**, **10q**, **12k** and **13e** have been obtained in synthetically useful manner. Such intermediates are of immense synthetic significance in the synthesis of *meso*-linked novel porphyrinoids [38] and other categories of cyclic conjugated entities. Incidentally, direct condensation of terephthaldehyde [30b,39] with mixtures of thiophene, furan or indole furnish corresponding symmetrical *meso*-linked bis(heterocyclyl)methane derivatives bearing identical bis(heterocyclyl)methane units on either side of the bridge.

3. Conclusion

In summary, we have demonstrated an efficient condensation of electron rich heterocycles with a variety of aldehydes using Amberlyst 15 catalyst, without using solvent in the reaction. The most attractive feature of this catalytic method is the facile condensation of electron rich heterocycles with aldehydes using justified stoichiometric quantities. In addition, the Amberlyst 15 catalyzed protocol is of potential industrial significance as many of the products obtained herein are of commercial significance besides the condensation protocol depicted higher yields of the products, recyclability and environmental friendliness of the catalyst, short reaction times, and overall practicability of the process as it does not require any specialized equipment or inert atmospheric conditions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2011.07.007.

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