

# (Aryl)(2-furyl)alkanes and their derivatives, 20.<sup>1</sup>

## Synthesis of symmetric bis- and tris(2-furyl)methanes

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### Abstract

New methods for the synthesis of symmetric 5,5'-disubstituted bis- and 5,5',5''-trisubstituted tris(2-furyl)methanes have been developed. Symmetric bis(2-furyl)methanes were prepared from 5-substituted 2-furylmethanols in the presence of concentrated perchloric acid. The attempted synthesis of (aryl)[bis(2-furyl)]methanes from (aryl)(2-furyl)methanols in the presence of acid catalysts failed. The reaction of 5-substituted 2-furaldehydes with ethylene glycol in the presence of strong acid catalysts led to tris(2-furyl)methanes. Plausible mechanisms of these transformations are discussed.

**Keywords:** Furylalkanes, bis(2-furyl)methanes, tris(2-furyl)methanes, furaldehydes

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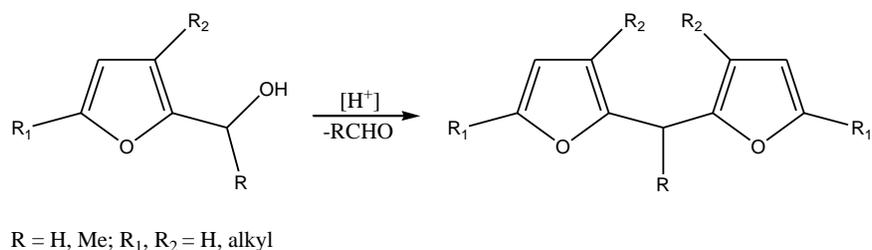
### Introduction

In recent years many research groups focused their attention on the development of convenient approaches to unsymmetric (furyl)(hetaryl)methanes.<sup>2-5</sup> However, the synthesis of symmetric bis(2-furyl)methanes is still an important and challenging goal. The availability of these compounds continues to be of interest because they are industrially important. In particular, some bis(2-furyl)methanes can be used as monomers and cross-linking reagents in polymer manufacturing.<sup>6-9</sup> Our research in the area of the chemistry of (aryl)(2-furyl)methanes led us to elaborate convenient routes to derivatives of bis- and tris(2-furyl)methanes.<sup>10</sup>

#### **Bis(2-furyl)methanes.**

The self-condensation of furfuryl alcohols is a useful and interesting method for the synthesis of symmetric bis(2-furyl)methanes. The acid-promoted oligomerization of furfuryl alcohol gives a mixture of products, among those bis(2-furyl)methane has been isolated in low yield.<sup>11</sup> It has been also found that the reaction of (5-aminomethyl-2-furyl)methanol with 5.1 M hydrochloric

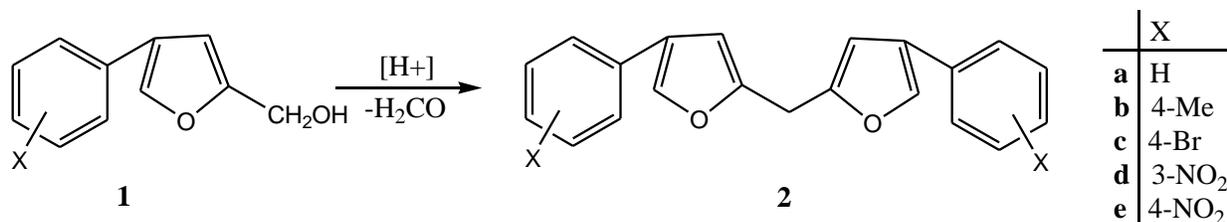
acid furnished bis(5-aminomethyl-2-furyl)methane as a minor product.<sup>12</sup> Hydrothermolysis of (5-methyl-2-furyl)methanol at 300 °C and pH ~ 7 produced bis(5-methyl-2-furyl)methane in 15% yield.<sup>13</sup> All these formations of bis(2-furyl)alkanes occur as side reactions, and the low yields make these reactions less important for synthetic purposes. On the other hand, there are also reports of excellent yields for the preparation of bis(2-furyl)alkanes from 3-, 5-alkyl-, and 3,5-dialkyl-substituted 2-furylalkanols (Scheme 1). These reactions proceed in the presence of polyphosphoric acid,<sup>14</sup> silver(I) ions or trichloroacetic acid.<sup>15</sup> Some bis(5-aryl-2-furyl)methanes have been reported to show tuberculostatic activity, but these compounds were obtained only as by-products of some reactions.<sup>16</sup> Therefore, the search for new approaches and better reaction conditions for the preparation of symmetric bis(2-furyl)methanes remains an interesting task.



Scheme 1

## Results and Discussion

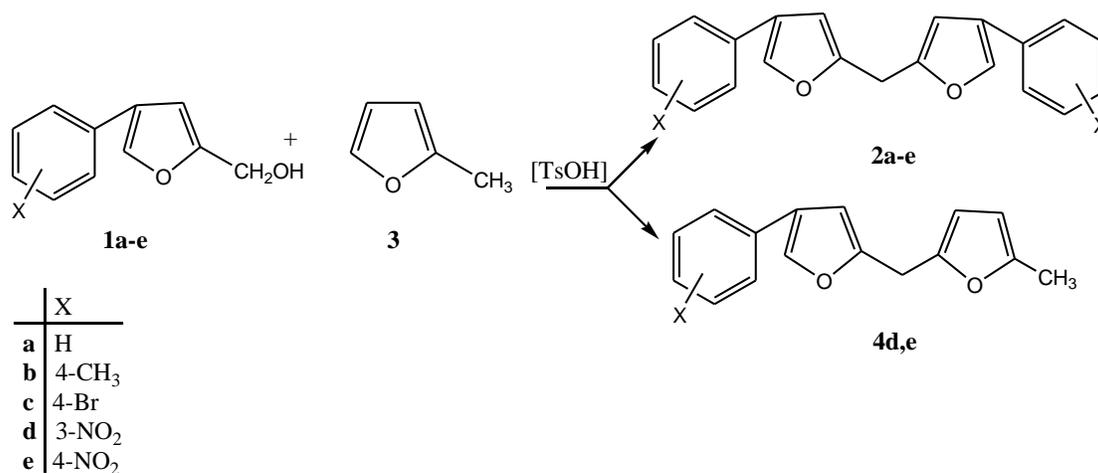
We have tried to develop a simple and efficient synthetic approach to symmetric bis(2-furyl)alkanes based on the self-condensation of 2-furylmethanols under acidic conditions. As starting materials (5-aryl-2-furyl)methanols (1) were chosen, and we found that these alcohols in dioxane solution and in the presence of perchloric acid were transformed into bis(5-aryl-2-furyl)methanes (2) (Scheme 2).



Scheme 2

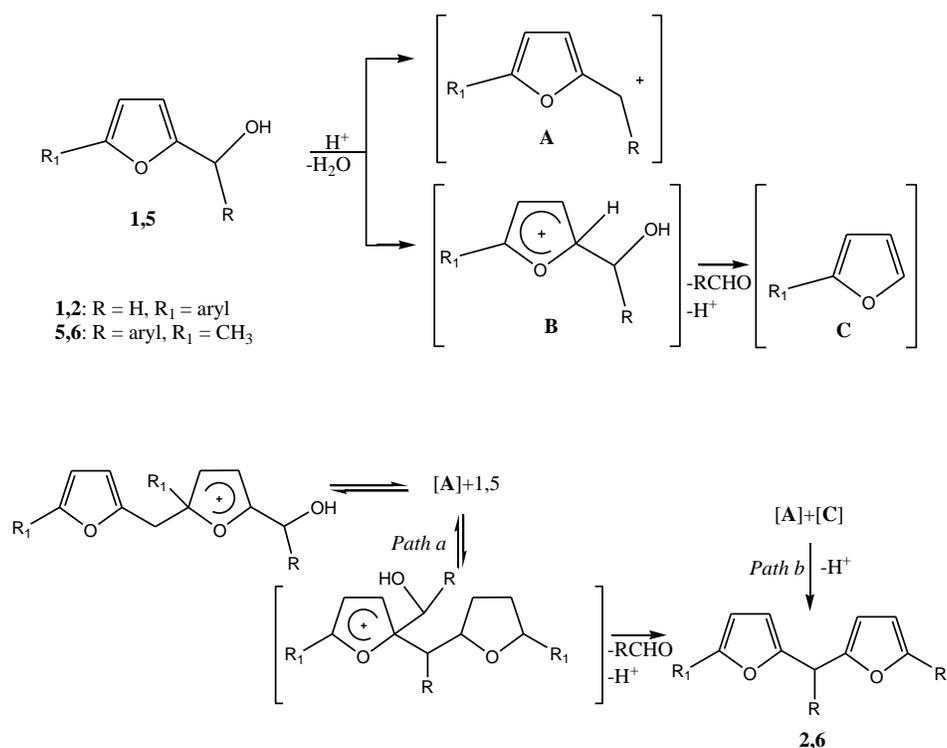
Bis(5-aryl-2-furyl)methanes (2) were also obtained when benzene solutions of alcohols 1 and 2-methylfuran 3 (molar ration 1 : 1.5-2.0) were treated with catalytic amounts of *p*-toluenesulfonic acid (Scheme 3). Under these reaction conditions alcohols 1a-c afforded only the symmetric

condensation products bis(5-aryl-2-furyl)methanes 2a-c. By contrast, the reaction of alcohols 1d,e with 2-methylfuran (3) in benzene solution and in the presence of catalytic amounts of *p*-toluenesulfonic acid resulted in a mixture of symmetric and unsymmetric condensation products, bis(5-aryl-2-furyl)methanes (2d,e) and (5-aryl-2-furyl)(5-methyl-2-furyl)methanes (4d,e), respectively. The product mixtures were separated by column chromatography and provided 2d (12%), 4d (43%) and 2e (8%), 4e (45%), respectively. Even a tenfold excess of 2-methylfuran 3 in this reaction did not prevent the formation of 2d,e in addition to 4d,e. The formation of bis(5-aryl-2-furyl)methanes 2 in this reaction may be explained by the acid-induced self-condensation reaction of (5-aryl-2-furyl)methanols (1).



### Scheme 3

An analogous conversion of hetarylmethanols into bis(hetaryl)methanes has been described earlier by Balaban and co-workers<sup>14</sup> for furan derivatives and by Jackson *et al.* for 2-pyrrolylmethanols.<sup>17,18</sup> Two conceivable pathways, *Path a* or *Path b* (as outlined in Scheme 4) may explain the formation of bis(2-furyl)alkanes from 2-furylmethanols.<sup>14,15</sup>



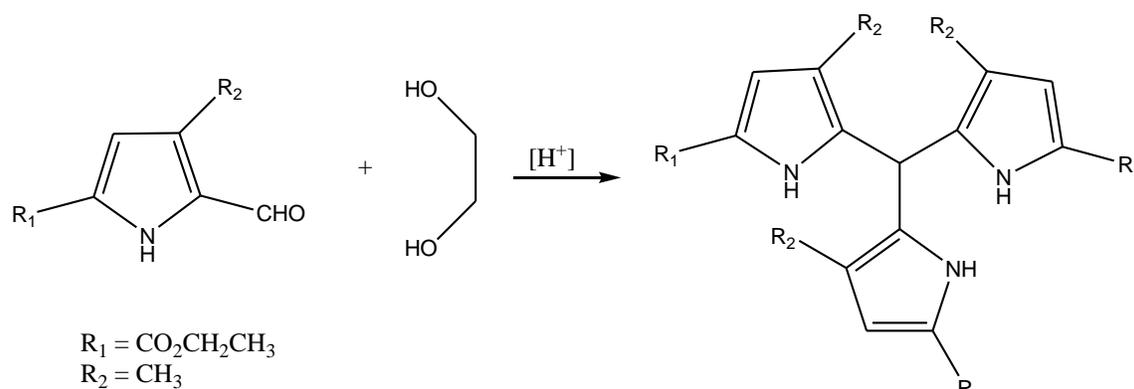
#### Scheme 4

We could not find any report in the literature on the formation of aryl[bis(2-furyl)]methanes emerging from a self-condensation of aryl(2-furyl)methanols under acidic reaction conditions. It was anticipated (*cf.* Scheme 4) that protonation of aryl(5-methyl-2-furyl)methanol (5) would give rise to an aryl(2-furyl)methyl cation A ( $R = \text{aryl}, R^1 = \text{methyl}$ ); a conceivable alternative would be protonation at the 2-position of the furan ring forming the cation intermediate B ( $R = \text{aryl}, R^1 = \text{methyl}$ ), which, in turn, may undergo loss of araldehyde and after deprotonation provides the 2-methylfuran C as an intermediate. Conceivably, following either *Path a* or *Path b* aryl[bis(2-furyl)]methanes 6 may be formed. However, all attempts to convert aryl(5-methyl-2-furyl)methanols (5a-c) [For a  $X = H$ ; b  $X = \text{CH}_3$ ; c  $X = \text{OCH}_3$ ] with the aid of various acid catalyst [ $\text{HClO}_4$ ,  $\text{TsOH}$ ,  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ , Amberlyst 15, KU-2,  $\text{HCl}$  (gas),  $\text{H}_2\text{SO}_4$ ] into aryl[bis(2-furyl)]methanes 6a-c failed. Treatment of 5a-c with acid catalysts in benzene or dioxane solutions resulted only in tar production (possibly via the cation intermediate D after deprotonation of the presumed first-formed intermediate A (Scheme 5). However, when (5-methyl-2-furyl)phenylmethanol (5a) was treated with hydrochloric acid in ethanol solution the corresponding ethyl ether 7a was obtained, and this is taken as evidence of the intermediacy of cation A.



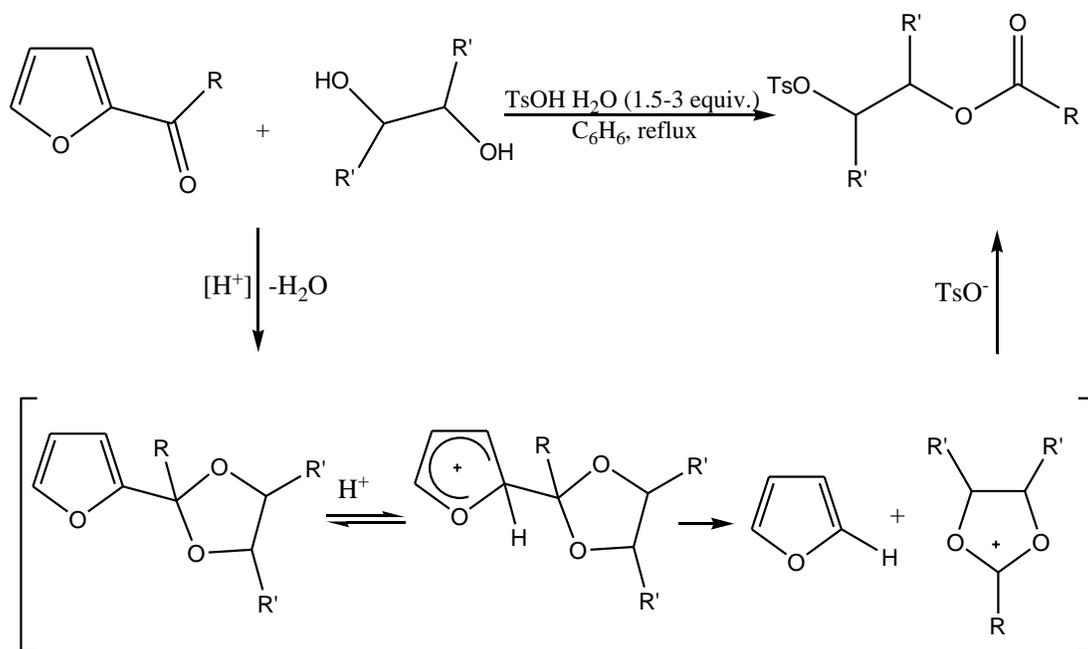
dioxolane 8b upon reaction with an electrophilic reagent such as trityl perchlorate or by perchloric acid (presumably, the latter may have been generated by the hydrolysis of trityl perchlorate induced by moisture from air or from the solvent used) according to Scheme 10 (*vide infra*). For the conversion of 8b into 9b, HClO<sub>4</sub> provides H<sup>+</sup>; alternatively, if Tr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> is the electrophilic reagent (H<sup>+</sup> is replaced by Tr<sup>+</sup>, and in this case, OH of the subsequent intermediates [in Scheme 10 their structures are placed in brackets] is to be exchanged by OTr).

An analogous conversion was described by Clezy *et al.*<sup>23</sup> These authors have discovered that the reaction of ethyl 5-formyl-4-methyl-1*H*-pyrrole-2-carboxylate with ethylene glycol in the presence of TsOH as catalyst led to the formation of a tris(1*H*-2-pyrrolyl)methane derivative instead of the expected acetal of the 1*H*-pyrrole-2-carbaldehyde (Scheme 7).



### Scheme 7

As West *et al.*<sup>24</sup> have found, the treatment of 2-acylfurans with 1,2-diols in the presence of one molar equivalent of TsOH•H<sub>2</sub>O does not furnish the desired ketal products. Instead, the isolated products were 1-*O*-acyl-2-*O*-(4-toluenesulfonyl) derivatives of the 1,2-diol reactants. The authors explain the formation of these products as the result of the protonation of the first-formed ketal intermediate, a 2-(2-furyl)[1,3]dioxolane derivative. Protonation of the furan moiety of this intermediate is presumed to be followed by the formation of furan and a [1,3]dioxolan-2-ylum cation. The latter intermediate reacts with tosylate under ring-opening to give the isolated ester (Scheme 8). For this process the name “protiodefuranation” has been coined.<sup>24</sup>



Scheme 8

With these literature reports in mind we tried to develop an efficient and simple route to symmetric 5,5',5''-trisubstituted tris(2-furyl)methanes 9. For this purpose we studied the influence of various acids as catalysts on the reaction of 5-methyl-2-furylaldehyde (10b) and ethylene glycol.<sup>22</sup> Both 2-(5-methyl-2-furyl)[1,3]dioxolane (8b) and tris(5-methyl-2-furyl)methane (9b) were formed (Scheme 9). The product ratio varied depending on the catalyst employed as was revealed by monitoring the reaction mixture by GLC: The weakly acidic KU-2 resin gave rise to mainly 8b and only traces of 9b; with the ion-exchanging resin Amberlyst 15 the ratio 8b : 9b depended of the amount of the catalyst employed: 10 mol% catalyst yielded a twenty-fold excess of 8b over 9b, whereas with 50 mol% catalyst the ratio was reversed, and only traces of 8b were formed beside the main product 9b. Similarly, boron trifluoride etherate furnished mainly 9b and only traces of 8b. With *p*-toluenesulfonic acid and perchloric acid the selectivity was less pronounced and the ratio 8b : 9b was found as 3 : 1 and 1 : 5, respectively.



Under otherwise unchanged reaction conditions the reaction of 5-methyl-2-furaldehyde 10b with 1,3-butanediol instead of ethylene glycol gave only a mixture of 4-methyl-2-(5-methyl-2-furyl)[1,3]dioxane and tris(5-methyl-2-furyl)methane 9b. All efforts to find suitable conditions for the formation of either 4-methyl-2-(5-methyl-2-furyl)[1,3]dioxane or tris(5-methyl-2-furyl)methane 9b failed. Moreover, the application of other 1,3-diols such as 2,4-pentanediol and 1-methyl-1,3-butanediol did not furnish the tris(2-furyl)methanes 9. Our results are in agreement with Clezy's report<sup>23</sup> on the failure in preparing symmetric tris(2-pyrrolyl)methanes upon treatment of 2-pyrrolicarbaldehydes with various substituted 1,3-butanediols in the presence of acid catalysts.

Furthermore, we investigated the reaction of 2-furaldehyde (10a), 5-ethyl-2-furaldehyde (10c), 5-bromo-2-furaldehyde (10d), and 5-aryl-2-furaldehydes (10e-i). The interaction between 2-furaldehyde (10a) and ethylene glycol in the presence of KU-2 resin or TsOH afforded 2-(2-furyl)[1,3]dioxolane (8a) (80% yield).<sup>25</sup> The utilisation of a stronger acid (hydrochloric acid, perchloric acid, boron trifluoride etherate) as catalyst resulted in the formation of tar probably as a result of polymerisation. Similar to the conversion of 5-methyl-2-furylaldehyde (10b) the reaction of 5-ethyl-2-furaldehyde (10c) with ethylene glycol furnished tris(5-ethyl-2-furyl)methane (9c) in a good yield. On the other hand, 5-bromo-2-furaldehyde (10d) did not yield tris(5-bromo-2-furyl)methane (9d) and furnished only 2-(5-bromo-2-furyl)[1,3]dioxolane (8d); obviously, the reaction did not proceed beyond this stage.

The preparation of tris(5-aryl-2-furyl)methanes (9, R = aryl) by traditional methods (similar to tris(5-methyl-2-furyl)methane)<sup>19,20</sup> requires 2-arylfurans as starting materials which are not easily accessible.

By contrast, the 5-aryl-2-furaldehydes (10e-i) are readily available from 2-furaldehyde by the Meerwein reaction,<sup>26</sup> and were employed for the reaction with ethylene glycol and Amberlyst 15. With 50 mol% of Amberlyst 15 the 5-aryl-2-furaldehydes (10e-h) were converted into tris(5-aryl-2-furyl)methanes (9e-h). 5-(4-Nitrophenyl)-2-furaldehyde (10i) was an exception.

Even with excess of Amberlyst 15 or with strong acids such as perchloric acid and boron trifluoride etherate the desired tris[5-(4-nitrophenyl)-2-furyl)methane (9i) was not produced, only 2-[5-(4-nitrophenyl)-2-furyl][1,3]dioxolane (8i) was obtained. With a reduced amount of 10-20 mol% Amberlyst 15 the 5-(nitrophenyl)-2-furaldehydes (10h,i) yielded the corresponding 2-[5-(nitrophenyl)-2-furyl][1,3]dioxolanes (8h,i).

In a separate experiment the isolated 2-[5-(3-nitrophenyl)-2-furyl][1,3]dioxolane (8h) was treated with Amberlyst 15 in refluxing benzene resulting in the conversion to tris[5-(3-nitrophenyl)-2-furyl]methane (9h).

This is in agreement with the proposed reaction path (Scheme 10) for the formation of 9 from 10 *via* the intermediate 8; as shown by this experiment the [1,3]dioxolane 8h is the precursor of tris[5-(3-nitrophenyl)-2-furyl]methane (9h).

## Conclusions

We have developed simple and convenient procedures for preparing novel symmetric 5,5''-disubstituted bis(2-furyl)methanes 2 and 5,5',5''-trisubstituted tris(2-furyl)methanes 9.

The former products 2 were prepared from 5-substituted 2-furylmethanols 1 with concentrated perchloric acid.

The latter products 9 arose from the reaction of 5-substituted 2-furaldehydes 10 with ethylene glycol in the presence of a strongly acidic catalysts.

Notable advantages of the described methods are the simple and mild reaction conditions as well as good product yields.

## Experimental Section

**General Procedures.** Melting points were determined on a Thomas capillary melting point apparatus. <sup>1</sup>H NMR spectra were recorded on a Tesla BS 487 (80 MHz) and on a Bruker AMX-400 spectrometer (400 MHz). Gas chromatography (GLC) was performed with a Chrom-5 equipped with a flame ionization detector using a column (2500 x 3 mm) with 5% carbowax coated on Chromaton N-AW-DMCS; the carrier gas was nitrogen. Thin layer chromatography (TLC) was carried out on aluminium backed silica plates Silufol UV 254. Elemental analyses were carried out at this Laboratory.

Compounds 1 were prepared by reduction of the corresponding 5-aryl-2-furaldehydes 10e-i with sodium borohydride.<sup>27</sup> 2-Methylfuran 3 and the 5-substituted 2-furaldehydes 10b-d were commercial products. The following starting materials were prepared according to the procedure reported in the literature: 5,<sup>28</sup> 8a,b,<sup>25</sup> 8d,<sup>29</sup> 5-aryl-2-furaldehydes 10a-i.<sup>26</sup> The physical data of tris(5-methyl-2-furyl)methane 9b are in agreement with those given in lit.<sup>19</sup>

Bis(5-aryl-2-furyl)methanes (2a-e)

**General procedure.** To a solution of (5-aryl-2-furyl)methanol (1a-e) (10 mmol) in dioxane (30-70 mL) was added HClO<sub>4</sub> (70%, 0.5-1.0 mL). As monitored by TLC the reaction was complete after 30-60 min. The reaction mixture was diluted with water (4-5 times the volume of the reaction mixture) and stirred until the separated oil turned crystalline. The precipitate formed was filtered off, washed with water, dried on air, and recrystallised from benzene-hexane mixtures after filtration of the hot solution through a layer of silica gel.

**Bis(5-phenyl-2-furyl)methane (2a).** Yield 70%; mp 78-79 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 4.05 (s, 2H, CH<sub>2</sub>), 6.13 (d, *J* = 3.2 Hz, 2H, 3-H<sub>fur</sub>), 6.52 (d, *J* = 3.2 Hz, 2H, 4-H<sub>fur</sub>), 7.12 - 7.70 (m, 10H<sub>ar</sub>). Anal. Calcd. for C<sub>21</sub>H<sub>16</sub>O<sub>2</sub>: C, 84.00; H, 5.33. Found: C, 84.06; H, 5.27.

**Bis[5-(4-methylphenyl)-2-furyl]methane (2b).** Yield 79%; mp 106-107 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 2.27 (s, 6H, CH<sub>3</sub>), 4.04 (s, 2H, CH<sub>2</sub>), 6.10 (d, *J* = 3.2 Hz, 2H, 3-H<sub>fur</sub>), 6.44 (d, *J* = 3.2

Hz, 2H, 4-H<sub>fur</sub>), 7.03, 7.14 (AA', 4H, 3-, 5-, 3', 5'-H<sub>ar</sub>), 7.41, 7.52 (BB', 4H, 2-, 6-, 2', 6'-H<sub>ar</sub>). Anal. Calcd. for C<sub>23</sub>H<sub>20</sub>O<sub>2</sub>: C, 84.15; H, 6.10. Found: C, 84.08; H, 6.17.

**Bis[5-(4-bromophenyl)-2-furyl]methane (2c).** Yield 76%; mp 160-161 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 4.03 (s, 2H, CH<sub>2</sub>), 6.13 (d, *J* = 3.2 Hz, 2H, 3-H<sub>fur</sub>), 6.50 (d, *J* = 3.2 Hz, 2H, 4-H<sub>fur</sub>), 7.42 (s, 8H<sub>ar</sub>). Anal. Calcd. for C<sub>21</sub>H<sub>14</sub>Br<sub>2</sub>O<sub>2</sub>: C, 55.02; H, 3.06. Found: C, 55.08; H, 3.00.

**Bis[5-(3-nitrophenyl)-2-furyl]methane (2d).** Yield 75%; mp 144-145 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 4.08 (s, 2H, CH<sub>2</sub>), 6.19 (d, *J* = 3.2 Hz, 2H, 3-H<sub>fur</sub>), 6.61 (d, *J* = 3.2 Hz, 2H, 4-H<sub>fur</sub>), 7.42-7.51 (m, 2H, 5-, 5'-H<sub>ar</sub>), 7.94-8.05 (m, 4H, 4-, 4', 6-, 6'-H<sub>ar</sub>), 8.32-8.39 (m, 2H, 2-, 2'-H<sub>ar</sub>). Anal. Calcd. for C<sub>21</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub>: C, 64.62; H, 3.59. Found: C, 64.53; H, 3.64.

**Bis[5-(4-nitrophenyl)-2-furyl]methane (2e).** The reaction of 5-(4-nitrophenyl)-2-furylmethanol (1e) was carried out at 40-50 °C to give 2e. Yield 71%; mp 175-176 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 4.13 (s, 2H, CH<sub>2</sub>), 6.26 (d, *J* = 3.2 Hz, 2H, 3-H<sub>fur</sub>), 6.76 (d, *J* = 3.2 Hz, 2H, 4-H<sub>fur</sub>), 7.61, 7.72 (AA', 4H, 2-, 6-, 2', 6'-H<sub>ar</sub>), 8.10, 8.21 (BB', 4H, 3-, 5-, 3', 5'-H<sub>ar</sub>). Anal. Calcd. for C<sub>21</sub>H<sub>14</sub>N<sub>2</sub>O<sub>6</sub>: C, 64.62; H, 3.59. Found: C, 64.66; H, 3.53.

### Reaction of 5-aryl-2-furylmethanols (1d,e) with 2-methylfuran (3). General procedure

2-Methylfuran (3) (15-20 mmol) was dissolved in a solution of 5-aryl-2-furylmethanol (1d,e) (10 mmol) in benzene (30-70 mL), and a catalytic amount of TsOH was added. The reaction mixture was stirred until all 1d,e was consumed (monitored by TLC). The benzene solution was washed with aqueous NaHCO<sub>3</sub> solution, with water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure. Compounds 2a-c were recrystallised from the mixture benzene:hexane (1:4) to give pure samples in 60, 63 and 66 % yield, respectively. For alcohols 1d,e the residue was separated by column chromatography (silica gel Silufol, 40-100 mesh; eluent: hexane / chloroform 1 : 2) to give pure products 2d (12%) and 2e (8%), respectively; in addition, 4d (43 %) and 4e (45 %) were isolated.

**(5-Methyl-2-furyl)[5-(3-nitrophenyl)-2-furyl]methane (4d).** Yield 43%; mp 77-77.5 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 2.22 (s, 3H, CH<sub>3</sub>), 3.95 (s, 2H, CH<sub>2</sub>), 5.82 (d, *J* = 3.2 Hz, 1H, 4-H<sub>fur</sub>), 5.93 (d, *J* = 3.2 Hz, 1H, 3-H<sub>fur</sub>), 6.10 (d, *J* = 3.2 Hz, 1H, 3-H'<sub>fur</sub>), 6.60 (d, *J* = 3.2 Hz, 1H, 4-H'<sub>fur</sub>), 7.23-8.33 (m, 4H, H<sub>ar</sub>). Anal. Calcd. for C<sub>16</sub>H<sub>13</sub>NO<sub>4</sub>: C, 67.85, H, 4.59; Found: C, 67.99, H, 4.53;.

**(5-Methyl-2-furyl)[5-(4-nitrophenyl)-2-furyl]methane (4e).** Yield 45%; mp 95-96 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 2.27 (s, 3H, CH<sub>3</sub>), 4.05 (s, 2H, CH<sub>2</sub>), 5.89 (d, *J* = 3.2 Hz, 1H, 4-H<sub>fur</sub>), 6.00 (d, *J* = 3.2 Hz, 1H, 3-H<sub>fur</sub>), 6.28 (d, *J* = 3.2 Hz, 1H, 3-H'<sub>fur</sub>), 7.02 (d, *J* = 3.2 Hz, 1H, 4-H'<sub>fur</sub>), 7.72, 7.83 (AA', 2H, 2-, 6-H<sub>ar</sub>), 8.15, 8.26 (BB', 2H, 3-, 5-H<sub>ar</sub>). Anal. Calcd. for C<sub>16</sub>H<sub>13</sub>NO<sub>4</sub>: C, 67.85, H, 4.59; Found: C, 67.93, H, 4.64.

### Reaction of Aryl(2-furyl)methanols (5a-c) with Acid Catalysts. General procedure

To a solution of aryl(5-methyl-2-furyl)methanols (5a-c) (10 mmol) in benzene (20-30 mL) and acid catalyst (HClO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, TsOH, BF<sub>3</sub>•Et<sub>2</sub>O, hydrochloric acid or 10-20 % of KU-2 resin or

10-20 % Amberlyst 15 was added. The reaction mixture was kept at rt for 12-36 h or at reflux for 1-3 h. Thereafter, the reaction mixture was washed with NaHCO<sub>3</sub> solution, water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was completely evaporated, and residue was dissolved in benzene (2 mL) and analysed by GLC. No aryl(5-methyl-2-furyl)methanes 6a-c were detected using authentic samples<sup>19</sup> for comparison.

**2-[(Ethoxy)phenylmethyl]-5-methylfuran (7a).** To a solution of (5-methyl-2-furyl)phenylmethanol (5a) (1.88 g, 10 mmol) in ethanol (25 mL) hydrochloric acid (0.5 mL) was added. The reaction mixture was kept at rt for 4 h, diluted with water (100 mL) and extracted with dichloromethane (3 x 30 mL). The combined organic layers were washed with NaHCO<sub>3</sub> solution, water, and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was completely evaporated, and the residue was purified by column chromatography (silica gel, eluent hexane/chloroform 2:1); the main fraction afforded a pale yellow oil 7a (0.86 g, 40%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 1.33 (t, *J* = 7.2 Hz, 3H, OCH<sub>2</sub>CH<sub>3</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 3.55 (dq, *J* = 19.6 Hz, *J* = 7.2 Hz, 2H, OCH<sub>A</sub>HCH<sub>3</sub>), 3.66 (dq, *J* = 19.6 Hz, *J* = 7.2 Hz, 2H, OCH<sub>H<sub>B</sub></sub>CH<sub>3</sub>), 5.39 (s, 1H, CH), 5.91 (d, *J* = 3.2 Hz, 1H, 4-H<sub>fur</sub>), 6.02 (d, *J* = 3.2 Hz, 1H, 3-H<sub>fur</sub>), 7.35-7.68 (m, 5H, Ph). Anal. Calcd for C<sub>14</sub>H<sub>16</sub>O<sub>2</sub>: C, 77.78; H, 7.41; Found: C, 78.00; H, 7.33.

**Reaction of 5-methyl-2-furaldehyde (10b) with ethylene glycol and acid catalysts.** A mixture of 5-methyl-2-furaldehyde (10b) (1.1 g, 10 mmol), ethylene glycol (0.3 g, 11 mmol), benzene (15 mL), and an acid catalyst such as ion-exchange resin KU-2 (0.1 g), Amberlyst 15 (0.1 or 0.5 g), TsOH (0.025 g), HClO<sub>4</sub> (70%, 0.05 mL), or BF<sub>3</sub> • Et<sub>2</sub>O (0.05 mL) was refluxed using a Dean-Stark trap. The reaction mixture was filtered (to remove KU-2 or Amberlyst 15) or washed with NaHCO<sub>3</sub> solution and water, dried over Na<sub>2</sub>SO<sub>4</sub>. Most of the solvent was evaporated to reduce the volume to about 2 mL, and the residue was analyzed by GLC using authentic samples of 9b<sup>19</sup> and 8b.<sup>25</sup> The ratio of 8b : 9b was determined from the respective peak areas (*cf.* Results and Discussion section).

**2-(2-Furyl)[1,3]dioxolane (8a).** A mixture of 2-furaldehyde (10a) (1.92 g, 20 mmol), ethylene glycol (0.6 g, 22 mmol), benzene (30 mL), and an acid catalyst such as ion-exchange resin KU-2 (0.2 g), or TsOH (0.05 g) was refluxed using a Dean-Stark trap for 6h. The reaction mixture was filtered (to remove KU-2) or washed with NaHCO<sub>3</sub> solution and water (for TsOH), dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was distilled *in vacuo* to yield 2-(2-furyl)[1,3]dioxolane (8a) as a colorless liquid (1.12 g, 80%). Bp 89-90 ° C/15 mm (lit.<sup>25</sup> 89 ° C/15 mm).

**[2-(5-Bromo-2-furyl)][1,3]dioxolane (8d).** A mixture of 5-bromo-2-furaldehyde (10d) (1.75 g, 10 mmol), ethylene glycol (0.3 g, 11 mmol), benzene (15 mL), and Amberlyst 15 (0.5 g) or HClO<sub>4</sub> (70%, 0.05 mL) or BF<sub>3</sub>•Et<sub>2</sub>O (0.05 mL) was refluxed for 5-7 h using a Dean-Stark trap. The reaction mixture was filtered (to remove Amberlyst 15) or washed with NaHCO<sub>3</sub> solution and water, dried over Na<sub>2</sub>SO<sub>4</sub>. Most of the solvent was evaporated to reduce the volume to about 2 mL, and this reaction mixture was analyzed by GLC using authentic samples of 8d<sup>29</sup> and 10d;

only 8d and 10d were detected, and the ratio of 9 : 1 was determined from the respective peak areas.

### 2-(5-Aryl-2-furyl)[1,3]dioxolanes (8h,i). General procedure

A mixture of 5-aryl-2-furaldehyde (10h,i)<sup>26</sup> (10 mmol), ethylene glycol (0.32 g, 12 mmol), benzene (40-70 mL) and Amberlyst 15 (10-20 mol% of aldehyde) was vigorously stirred and refluxed for 3-8 h using a Dean-Stark trap. After the catalyst was filtered off, the solvent was evaporated *in vacuo*; the residue was purified by column chromatography (silica gel, eluent hexane/dichloromethane 2:1) to yield the products 8h,i.

**2-[5-(3-Nitrophenyl)-2-furyl][1,3]dioxolane (8h).** Yield 50%; mp 82-83 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 4.01-4.13 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>O), 5.94 (s, 1H, CH), 6.51 (d, *J* = 3,2 Hz, 1H, 3-H<sub>fur</sub>), 6.71 (d, *J* = 3,2 Hz, 1H, 4-H<sub>fur</sub>), 7.48-7.98 (m, 3H, H<sub>ar</sub>), 8.40-8.47 (m, 1H, H<sub>ar</sub>). Anal Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>5</sub>: C, 59.77; H, 4.22; Found: C, 59.70; H, 4.28.

**2-[5-(4-Nitrophenyl)-2-furyl][1,3]dioxolane (8i).** Yield 47%; mp 121-122 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>), δ 4.00-4.11 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>O), 5.93 (s, 1H, CH), 6.51 (d, *J* = 3,2 Hz, 1H, 3-H<sub>fur</sub>), 6.76 (d, *J* = 3,2 Hz, 1H, 4-H<sub>fur</sub>), 7.66, 7.77 (AA', 2H, 2-, 6-H<sub>ar</sub>), 8.10, 8.21 (BB', 2H, 3-, 5-H<sub>ar</sub>). Anal Calcd for C<sub>13</sub>H<sub>11</sub>NO<sub>5</sub>: C, 59.77; H, 4.22; Found: C, 59.64; H, 4.30.

**Tris(5-ethyl-2-furyl)methane (9c).** A mixture of 5-ethyl-2-furaldehyde (10c) (2.48 g, 20 mmol), ethylene glycol (0.6 g, 22 mmol) Amberlyst 15 (1.2 g, 50 mol% of aldehyde) in benzene (30 mL) was refluxed using a Dean-Stark trap for 5-7 h. The reaction mixture was filtered (to remove Amberlyst 15) and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated and the residue was distilled *in vacuo* to yield 9c as viscous dark-yellow oil (1.27 g, 84 %). <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 1.17 (t, *J* = 7.8 Hz, 9H, CH<sub>2</sub>CH<sub>3</sub>), 2.55 (q, *J* = 7.8 Hz, 6H, CH<sub>2</sub>CH<sub>3</sub>), 5.18 (s, 1H, CH), 5.75 (s, 6H, H<sub>fur</sub>). Anal. Calcd for C<sub>19</sub>H<sub>22</sub>O<sub>3</sub>: C, 76.51; H, 7.38; Found: C, 76.62; H, 7.23.

### Tris(5-aryl-2-furyl)methanes (9e-h)

#### Method A

A mixture of 5-aryl-2-furaldehyde (10e-h)<sup>26</sup> (10 mmol), ethylene glycol (0.32 g, 12 mmol), benzene (40-70 mL) and Amberlyst 15 (50 mol% with respect to 10e-h) was vigorously stirred and refluxed for 6-20 h using a Dean-Stark trap until 10e-h was consumed (monitored by TLC). After the catalyst was filtered off, the solvent was evaporated *in vacuo*, and the residue was purified by column chromatography (on silica gel, eluent chloroform / hexane 2:3) to yield the products 9e-h.

**Tris(5-phenyl-2-furyl)methane (9e).** Yield 92%; mp 161-162 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 5.67 (s, 1H, CH), 6.22 (d, *J* = 3.2 Hz, 3H, 3-H<sub>fur</sub>), 6.57 (d, *J* = 3.2 Hz, 3H, 4-H<sub>fur</sub>), 7.12 - 7.70 (m, 15H<sub>ar</sub>). Anal. Calcd. for C<sub>31</sub>H<sub>22</sub>O<sub>3</sub>: C, 84.16; H, 4.97. Found: C, 84.09; H, 5.03.

**Tris[5-(4-methylphenyl)-2-furyl]methane (9f).** Yield 86%; mp 139-140 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 2.27 (s, 9H, CH<sub>3</sub>), 5.59 (s, 1H, CH), 6.08 (d, *J* = 3.2 Hz, 3H, 3-H<sub>fur</sub>), 6.41 (d, *J* = 3.2 Hz, 3H, 4-H<sub>fur</sub>), 6.95, 7.05 (AA', 4H, 3-, 5-, 3''-, 5''-, 3'''-, 5'''-H<sub>ar</sub>), 7.36, 7.46 (BB', 6H, 2-, 6-, 2'-, 6'-, 2''-, 6''-H<sub>ar</sub>). Anal. Calcd. for C<sub>34</sub>H<sub>28</sub>O<sub>3</sub>: C, 84.12; H, 5.77. Found: C, 84.19; H, 5.71.

**Tris[5-(4-bromophenyl)-2-furyl]methane (9g).** Yield 93%; mp 110-111 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 5.58 (s, 1H, CH), 6.14 (d, *J* = 3.2 Hz, 3H, 3-H<sub>fur</sub>), 6.48 (d, *J* = 3.2 Hz, 3H, 4-H<sub>fur</sub>), 7.38 (s, 12H, H<sub>ar</sub>). Anal. Calcd. for C<sub>31</sub>H<sub>19</sub>Br<sub>3</sub>O<sub>3</sub>: C, 54.79; H, 2.80. Found: C, 54.82; H, 2.69.

**Tris[5-(3-nitrophenyl)-2-furyl]methane (9h).** Yield 90%; mp 118-119 °C. <sup>1</sup>H NMR (80 MHz, CDCl<sub>3</sub>): δ 5.74 (s, 1H, CH), 6.32 (d, *J* = 3.2 Hz, 3H, 3-H<sub>fur</sub>), 6.73 (d, *J* = 3.2 Hz, 3H, 4-H<sub>fur</sub>), 7.47-8.07 (m, 9H, H<sub>ar</sub>), 8.38-8.42 (m, 3H, H<sub>ar</sub>). Anal. Calcd. for C<sub>31</sub>H<sub>19</sub>N<sub>3</sub>O<sub>9</sub>: C, 64.36; H, 3.29. Found: C, 64.43; H, 3.33.

**Tris[5-(3-nitrophenyl)-2-furyl]methane (9h)**

## Method B

A mixture of 2-[5-(3-nitrophenyl)-2-furyl][1,3]dioxolane (8h) (2.61 g, 10 mmol) and Amberlyst 15 (0.5 g, 20 % of aldehyde) in benzene (50 mL) was refluxed for 5 h. After the catalyst was filtered off, the solvent was evaporated *in vacuo*. The residue was dissolved in a mixture of benzene/hexane 1:4 and the hot solution was filtered through a pad of silica gel and kept to crystallise to yield 9h as a yellow powder (1.75 g, 92 %).

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