

Furyl(aryl)alkanes and Their Derivatives. 19*. Synthesis of Benzofuran Derivatives via 2-Hydroxyaryl-R-(5-methylfur-2-yl)methanes. Reaction of Furan Ring Opening - Benzofuran Ring Closure Type

Andrey V. Gutnov¹, Alexander V. Butin^{2**}, Vladimir T. Abaev¹, Gennadij D. Krapivin³ and Valerij E. Zavodnik⁴

¹Department of Organic Chemistry, North-Ossetian State University, Vatutina 46, Vladikavkaz, 362025, Russia. E-mail: ria@rno.ssc.ac.ru

²Research Laboratory of Furan Chemistry, Kuban State Technological University, Moskovskaya 2, Krasnodar, 350072, Russia. E-mail: nemol@kubstu.ru

³Department of Organic Chemistry, Kuban State Technological University, Moskovskaya 2, Krasnodar, 350072, Russia. E-mail: organics@kubstu.ru

⁴X-Ray Laboratory, Karpov Institute of Physical Chemistry, Vorontsovo pole 10, Moscow, 103064, Russia. E-mail: zaval@cc.nifhi.ac.ru

* Last report see [1].

**Author to whom correspondence should be addressed.

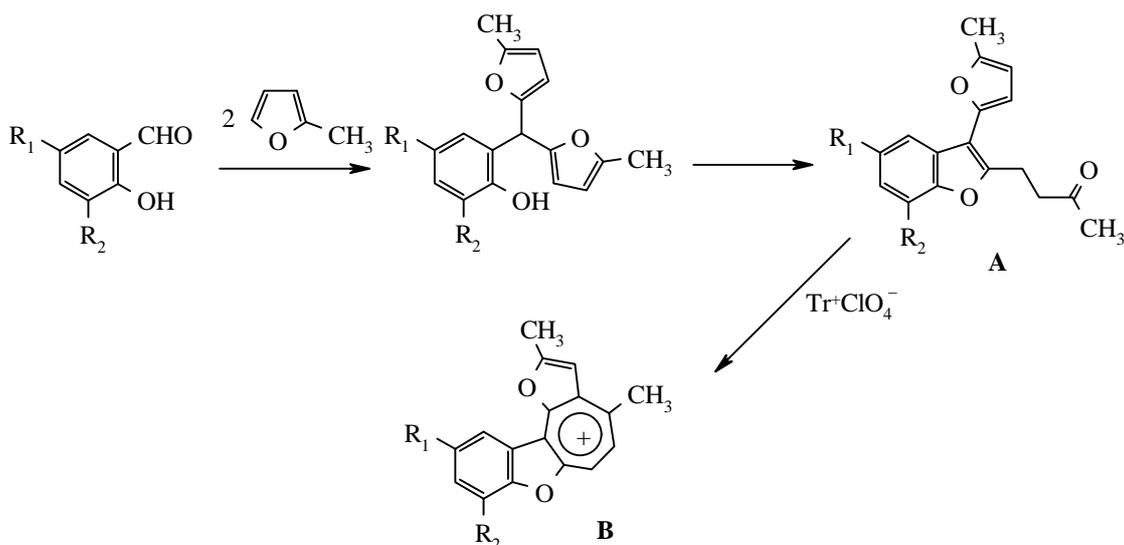
Received: 6 June 1999 / Accepted: 28 June 1999 / Published: 17 July 1999

Abstract: 2-Hydroxyaryl(5-methylfur-2-yl)alkanes synthesized by alkylation of 2-methylfuran with various 2-hydroxybenzylic alcohols, were rearranged into corresponding 3-R-benzo[b]furan derivatives by treatment with ethanolic HCl solution. These compounds can not be transformed into dibenzoxazulenium salts.

Keywords: 2-Hydroxybenzylic alcohols, 2-methylfuran, 2-hydroxyaryl(5-methylfur-2-yl)alkanes, 3-R-benzo[b]furans, recyclization.

Introduction

As it was shown by the authors in previous publications, 2-hydroxyaryl-bis(5-methylfur-2-yl)methanes, which are readily available by sylvane and salicylaldehydes condensation, catalyzed by trimethylchlorosilane or boric acid [2], undergo a rearrangement to 3-(5-methylfur-2-yl)-2-(3-oxobutyl)benzo[b]furan derivatives **A** by treatment with ethanolic hydrogen chloride solution (Scheme 1) [3]. The latter compounds can serve as precursors for benzo[b]furo[2,3-h]-1-oxazulenium salts **B** both by trityl perchlorate oxidation [4] and by disproportionation in the presence of perchloric acid [5]:



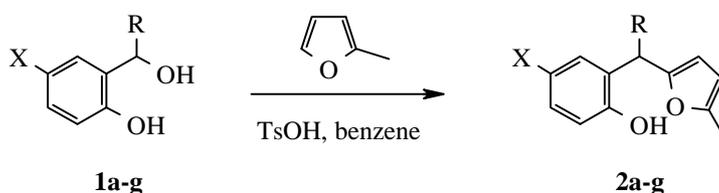
Scheme 1.

Previous results were summarized in review [6].

In the present work we attempt to extend the scope of such reactions.

Results and Discussion

Starting from substituted 2-hydroxybenzylic alcohols **1a-g** corresponding 2-hydroxyaryl-R-(5-methylfur-2-yl)alkanes were obtained:



Scheme 2.

When the condensation step was conducted in the presence of a highly acid, ion-exchange resin Amberlyst-15 or boric acid in boiling benzene the reaction did not go to completion. On the other hand the corresponding methanes **2a-g** were obtained quantitatively (Table 1) by refluxing the reagents in benzene with a catalytic amount of p-toluenesulfonic acid and with a Dean-Stark trap. The structure was proved by ^1H NMR spectra (Table 2). IR-spectra of these compounds contain the characteristic bands of absorption of valent vibrations of the OH group.

Table 1. Characterization of compounds **2a-g**.

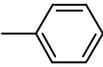
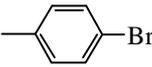
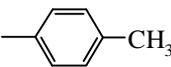
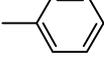
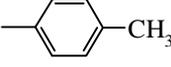
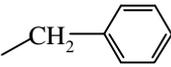
Comp	R	X	Formula, M_r	W_i (calc.)%		Yield %	IR-spectra cm^{-1} (bs, OH)
				W_i (found)%			
				C	H		
2a		CH_3	$\text{C}_{19}\text{H}_{18}\text{O}_2$ 278.35	<u>82.08</u> 81.99	<u>6.58</u> 6.52	99	3560
2b		CH_3	$\text{C}_{19}\text{H}_{17}\text{BrO}_2$ 357.25	<u>63.92</u> 63.88	<u>4.75</u> 4.80	99	3540
2c		CH_3	$\text{C}_{20}\text{H}_{20}\text{O}_2$ 292.38	<u>82.08</u> 82.16	<u>6.86</u> 6.89	98	3540
2d		H	$\text{C}_{18}\text{H}_{16}\text{O}_2$ 264.32	<u>81.77</u> 81.79	<u>6.16</u> 6.10	98	3560
2e		H	$\text{C}_{19}\text{H}_{18}\text{O}_2$ 278.35	<u>82.05</u> 81.99	<u>6.54</u> 6.52	99	3550
2f		CH_3	$\text{C}_{20}\text{H}_{20}\text{O}_2$ 292.38	<u>82.13</u> 82.16	<u>6.84</u> 6.89	97	3530
2g	$-\text{CH}_2\text{CH}_3$	CH_3	$\text{C}_{15}\text{H}_{18}\text{O}_2$ 230.31	<u>78.27</u> 78.23	<u>7.99</u> 7.88	98	3440

Table 2. $^1\text{H-NMR}$ spectra of compounds **2a-g**.

Comp.	δ , ppm
2a	2.18 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 4.81 (bs, 1H, OH), 5.41 (s, 1H, CH), 5.67-5.87 (m, 2H, H_{Fur}), 6.62-7.34 (m, 8H, H_{Ar})
2b	2.15 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 4.59 (bs, 1H, OH), 5.40 (s, 1H, CH), 5.65 (d, $J = 3.2$ Hz, 1H, 3- H_{Fur}), 5.77 (d, $J = 3.2$ Hz, 1H, 4- H_{Fur}), 6.42-7.53 (m, 7H, H_{Ar})
2c	2.14 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 4.69 (bs, 1H, OH), 5.35 (s, 1H, CH), 5.62 (d, $J = 3.2$ Hz, 1H, 3- H_{Fur}), 5.74 (d, $J = 3.2$ Hz, 1H, 4- H_{Fur}), 6.48-7.19 (m, 7H, H_{Ar})
2d	2.17 (s, 3H, CH_3), 5.02 (bs, 1H, OH), 5.56 (s, 1H, CH), 5.73 (d, $J = 3.2$ Hz, 1H, 3- H_{Fur}), 5.81 (d, $J = 3.2$ Hz, 1H, 4- H_{Fur}), 6.60-7.53 (m, 9H, H_{Ar})
2e	2.18 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 4.98 (bs, 1H, OH), 5.50 (s, 1H, CH), 5.47 (d, $J = 3.2$ Hz, 1H, 3- H_{Fur}), 5.82 (d, $J = 3.2$ Hz, 1H, 4- H_{Fur}), 6.64-7.32 (m, 8H, H_{Ar})
2f	2.13 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 3.10 (d, $J = 7.0$ Hz, 1H, CH_2), 3.18 (d, $J = 7.0$ Hz, 1H, CH_2), 4.28 (t, $J = 7.0$ Hz, 1H, CH), 4.83 (bs, 1H, OH), 5.68 (d, $J = 3.2$ Hz, 1H, 4- H_{Fur}), 5.79 (d, $J = 3.2$ Hz, 1H, 3- H_{Fur}), 6.82-7.09 (m, 8H, H_{Ar})
2g	0.83 (t, $J=7.1$ Hz, 3H, CH_2CH_3), 1.23 (m, 2H, CH_2CH_3), 2.16 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 3.92 (d, $J_{\text{CH}}=7.5$ Hz, 1H, CH), 4.96 (bs, 1H, OH), 5.76 (d, $J = 3.2$ Hz, 1H, 3- H_{Fur}), 5.71 (d, $J_{3,4\text{Fur}}=3.2$ Hz, 1H, 4- H_{Fur}), 6.37-7.13 (m, 3H, H_{Ar})

The prepared methanes were transformed smoothly into corresponding benzofuran derivatives **3a-g** (Table 3) by treatment with ethanolic HCl solution (Scheme 3). The main feature of ^1H NMR spectra (Table 4) of these compounds is the absence of the peaks of furan protons and the presence of two signals from methylene protons $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$. IR spectra of these compounds have an intensive band of valent vibrations of the CO group in the field of 1700 cm^{-1} .

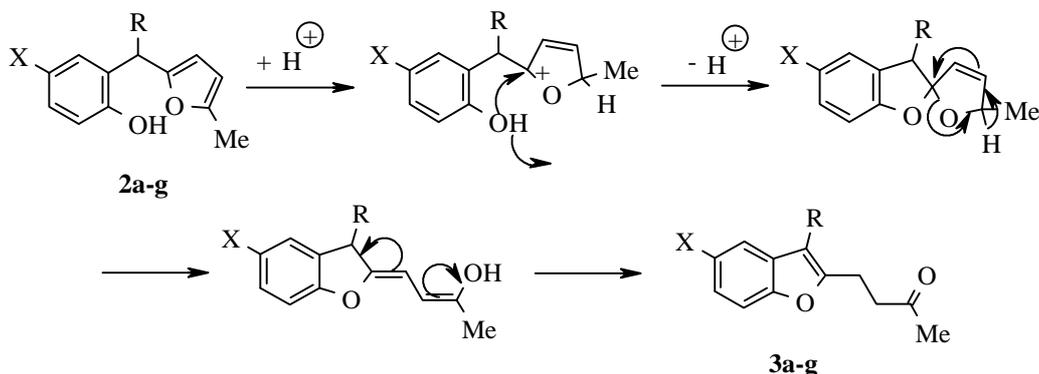
**Scheme 3.**

Table 3. Characterization of compounds **3a-g**.

Comp.	Formula, M _r	W _i (calc.)%		Yield %	M.p.(°C)
		W _i (found)%			
		C	H		
3a	C ₁₉ H ₁₈ O ₂ 278.35	<u>81.95</u>	<u>6.55</u>	92	57-58
		81.99	6.52		
3b	C ₁₉ H ₁₇ BrO ₂ 357.25	<u>63.92</u>	<u>4.77</u>	91	81-82
		63.88	4.80		
3c	C ₂₀ H ₂₀ O ₂ 292.38	<u>82.19</u>	<u>6.86</u>	95	oil
		82.16	6.89		
3d	C ₁₈ H ₁₆ O ₂ 264.32	<u>81.84</u>	<u>6.18</u>	95	39-40
		81.79	6.10		
3e	C ₁₉ H ₁₈ O ₂ 278.35	<u>82.05</u>	<u>6.55</u>	93	68-69
		81.99	6.52		
3f	C ₂₀ H ₂₀ O ₂ 292.38	<u>82.21</u>	<u>6.81</u>	90	41-42
		82.16	6.89		
3g	C ₁₅ H ₁₈ O ₂ 230.31	<u>78.12</u>	<u>7.80</u>	90	oil
		78.23	7.88		

Table 4. ¹H-NMR spectra of compounds **3a-g**.

Comp	δ, ppm
3a	2.09 (s, 3H, CH ₃ CO), 2.35 (s, 3H, CH ₃), 2.68-2.93 (m, 2H, β-CH ₂), 2.96-3.21 (m, 2H, α-CH ₂), 6.91-7.49 (m, 8H, H _{Bf} + H _{Ar})
3b	2.08 (s, 3H, CH ₃ CO), 2.34 (s, 3H, CH ₃), 2.67-2.91 (m, 2H, β-CH ₂), 2.92-3.16 (m, 2H, α-CH ₂), 6.98 (d, J = 8.1 Hz, 1H, 6-H _{Bf}), 7.20 (d, 1H, 4-H _{Bf}), 7.24 (d, J = 8.1 Hz, 1H, 7-H _{Bf}), 7.27 (d, J = 8.8 Hz, 2H, m-H _{Ar}), 7.52 (d, J = 8.8 Hz, 2H, o-H _{Ar})
3c	2.08 (s, 3H, CH ₃ CO), 2.34 (s, 6H, CH ₃), 2.67-2.92 (m, 2H, β-CH ₂), 2.95-3.20 (m, 2H, α-CH ₂), 6.90-7.40 (m, 7H, H _{Bf} + H _{Ar})
3d	2.07 (s, 3H, CH ₃ CO), 2.69-2.94 (m, 2H, β-CH ₂), 2.97-3.22 (m, 2H, α-CH ₂), 7.09-7.57 (m, 9H, H _{Bf} + H _{Ar})
3e	2.08 (s, 3H, CH ₃ CO), 2.34 (s, 3H, CH ₃), 2.69-2.94 (m, 2H, β-CH ₂), 2.97-3.22 (m, 2H, α-CH ₂), 7.07-7.56 (m, 8H, H _{Bf} + H _{Ar})
3f	2.06 (s, 3H, CH ₃ CO), 2.28 (s, 3H, CH ₃), 2.62-2.83 (m, 2H, β-CH ₂), 2.86-3.07 (m, 2H, α-CH ₂), 3.91 (s, 2H, CH ₂), 7.07-7.56 (m, 8H, H _{Bf} + H _{Ar})
3g	1.16 (t, J = 7.7 Hz, 3H, CH ₂ CH ₃), 2.10 (s, 3H, CH ₃ CO), 2.37 (s, 3H, CH ₃), 2.56 (k, J = 7.7 Hz, 2H, CH ₂ CH ₃), 2.60-2.85 (m, 2H, β-CH ₂), 2.87-3.02 (m, 2H, α-CH ₂), 6.94 (d, J = 8.1 Hz, 1H, 6-H _{Bf}), 7.16 (d, J = 8.1 Hz, 1H, 7-H _{Bf}), 7.18 (d, 1H, 4-H _{Bf})

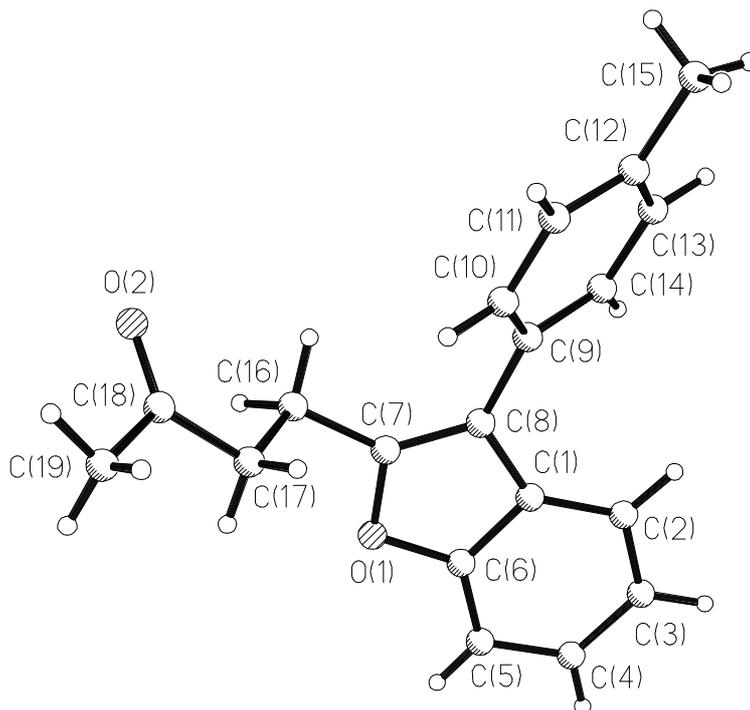


Figure 1. The X-Ray crystal structure of **3e**.

Table 5. Crystal data and structure refinement of **3e**.

Unit contents:	C(19)H(18)O(2)	
Space group:	P2(1)/c, Z = 4	
Crystal system:	monoclinic	
Unit cell dimensions:	a = 5.917(1)Å	Alpha = 90 deg.
	b = 25.393(2)Å	Beta = 101.08 (1) deg.
	c = 10.281(1)Å	Gamma = 90 deg.
Volume:	1515.9 (.6) Å ³	
Density (calculated):	1.220 g/cm ³	
Diffractometer:	Syntex P1	
Scan technique:	Theta/2*Theta	
Monochromator:	none	
Wave length:	.73 cm ⁻¹	
sin(Th)/WL(max):	.6168	
Lambda:	Mo (K-alpha)	
Number of reflections:	1898 I > 3.00*s (I)	
Programs:	SHELXTL	
Solution:	Direct method	
Final R factors:	R = .044 Rw = .050	
GOOF:	2.10	
Weight:	1/(sigma** (F) + .000439*F*F)	

The results of X-ray study of benzofuran **3e** monocrystal are given in Figure 1 and in Tables 5-7. No specific divergences from the bond lengths and valent angles in comparison with 3-furylbenzofuran **A** (data of X-ray study are given in [7]) are found except in the size of the dihedral angle between the benzofuran and the aromatic ring planes. In a molecule that contains a smaller furan cycle, this angle is 18°, and in a molecule **3e** with a larger phenyl cycle, this angle is 40°.

Table 6. Atom coordinates (10^{-4}) and temperature factors ($\text{Å}^2 \cdot 10^{-3}$).

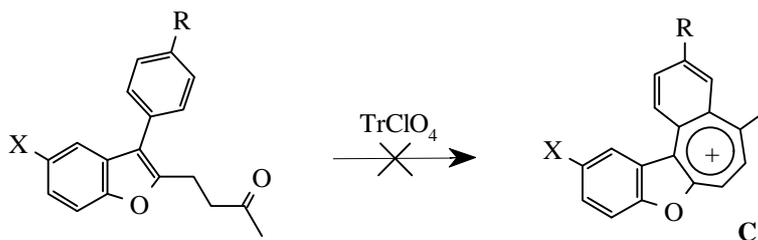
Atom	x	Y	z	Ueq
O(1)	2750 (2)	5797 (1)	4448 (1)	47 (1) *
O(2)	3568 (3)	4516 (1)	8262 (2)	82 (1) *
C(1)	650 (3)	6537 (1)	4561 (2)	39 (1) *
C(2)	-128 (4)	7038 (1)	4135 (2)	48 (1) *
C(3)	593 (5)	7253 (1)	3055 (2)	58 (1) *
C(4)	2105 (5)	6985 (1)	2408 (3)	59 (1) *
C(5)	2914 (5)	6490 (1)	2817 (2)	53 (1) *
C(6)	2145 (4)	6279 (1)	3873 (2)	42 (1) *
C(7)	1668 (4)	5760 (1)	5520 (2)	40 (1) *
C(8)	387 (3)	6190 (1)	5646 (2)	37 (1) *
C(9)	-892 (4)	6314 (1)	6703 (2)	37 (1) *
C(10)	7 (4)	6208 (1)	8029 (2)	45 (1) *
C(11)	-1124 (4)	6350 (1)	9019 (2)	49 (1) *
C(12)	-3226 (4)	6615 (1)	8741 (2)	48 (1) *
C(13)	-4144 (4)	6718 (1)	7423 (2)	46 (1) *
C(14)	-3021 (4)	6571 (1)	6421 (2)	42 (1) *
C(15)	-4417 (6)	6784 (2)	9839 (3)	68 (1) *
C(16)	2187 (4)	5266 (1)	6310 (2)	47 (1) *
C(17)	4624 (4)	5254 (1)	7116 (3)	48 (1) *
C(18)	5065 (4)	4816 (1)	8105 (2)	51 (1) *
C(19)	7478 (6)	4776 (1)	8881 (4)	73 (1) *

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U (i, j) tensor

Table 7. Bond lengths (Å) and angles (deg).

O(1) - C(6)	1.376 (2)	O(1) - C(7)	1.380 (3)
O(2) - C(18)	1.203 (3)	C(1) - C(2)	1.395 (3)
C(1) - C(6)	1.396 (3)	C(1) - C(8)	1.452 (3)
C(2) - C(3)	1.376 (4)	C(3) - C(4)	1.391 (4)
C(4) - C(5)	1.383 (3)	C(5) - C(6)	1.365 (3)
C(7) - C(8)	1.349 (3)	C(7) - C(16)	1.495 (3)
C(8) - C(9)	1.473 (3)	C(9) - C(10)	1.391 (3)
C(9) - C(14)	1.399 (3)	C(10) - C(11)	1.370 (3)
C(11) - C(12)	1.395 (3)	C(12) - C(13)	1.384 (3)
C(12) - C(15)	1.504 (4)	C(13) - C(14)	1.380 (3)
C(16) - C(17)	1.519 (3)	C(17) - C(18)	1.495 (3)
C(18) - C(19)	1.499 (4)		
C(6) - O(1) - C(7)	106.3 (2)	C(2) - C(1) - C(6)	118.1 (2)
C(2) - C(1) - C(8)	135.7 (2)	C(6) - C(1) - C(8)	106.1 (2)
C(1) - C(2) - C(3)	118.7 (2)	C(2) - C(3) - C(4)	121.3 (2)
C(3) - C(4) - C(5)	121.0 (2)	C(4) - C(5) - C(6)	116.8 (2)
O(1) - C(6) - C(1)	109.7 (2)	O(1) - C(6) - C(5)	126.2 (2)
C(1) - C(6) - C(5)	124.0 (2)	O(1) - C(7) - C(8)	112.2 (2)
O(1) - C(7) - C(16)	114.4 (2)	C(8) - C(7) - C(16)	133.5 (2)
C(1) - C(8) - C(7)	105.7 (2)	C(1) - C(8) - C(9)	125.7 (2)
C(7) - C(8) - C(9)	128.4 (2)	C(8) - C(9) - C(10)	121.9 (2)
C(8) - C(9) - C(14)	121.1 (2)	C(10) - C(9) - C(14)	117.0 (2)
C(9) - C(10) - C(11)	121.8 (2)	C(10) - C(11) - C(12)	121.2 (2)
C(11) - C(12) - C(13)	117.3 (2)	C(11) - C(12) - C(15)	120.8 (2)
C(13) - C(12) - C(15)	121.9 (2)	C(12) - C(13) - C(14)	121.7 (2)
C(9) - C(14) - C(13)	121.0 (2)	C(7) - C(16) - C(17)	112.8 (2)
C(16) - C(17) - C(18)	114.2 (2)	O(2) - C(18) - C(17)	121.7 (2)
O(2) - C(18) - C(19)	122.4 (2)	C(17) - C(18) - C(19)	115.9 (2)

As stated above (Scheme 1) 3-furylbenzofurans **A** can be transformed into oxazulenium cations **B** in high yields by oxidation with trityl perchlorate or by treatment with perchloric acid. Attempts to obtain analogues of these salts from 3-arylbenzofurans **3a-e** were unsuccessful. Neither oxidation by trityl perchlorate or chloroanil in methylene chloride nor treatment with perchloric acid in boiling dioxane gave the desired salts.



Scheme 4.

For the detection of the existing cation **B** features and the hypothetical cation **C** constitution (Scheme 4) their quantum-chemical calculation was conducted (preliminary optimization of geometry by a method MM+ and finally by a semiempirical method AM1). The outcomes of the cation **B** geometry calculation is shown in Figures 2, 4 and in Tables 8, 9, in which the result of the X-ray study of its monocrystal is also shown [4]. As it can be seen, values of interatomic spacing intervals and valent angles obtained by computational are in good agreement with experimental X-Ray data, except for the lengths of furan C-O bonds for which the calculation gives higher values. There are no intramolecular contacts causing sterical strain in the cation **B**.

Vice-versa, flat geometry of cation **C** (Figures 3, 5, Tables 10, 11) should be accompanied by strong intramolecular strain leading to a noticeable distortion of some valent angles and bond lengths as compared with standard values and with the corresponding values in cation **B**.

The main cause of sterical strain is intramolecular interaction H (23) ... H (26) (Figure 5). Interatomic spacing interval H (23) ... H (26) according to calculation is 1.628 Å, which is much less than the sum of their Van-der-Vaals radii. As a result, the bond lengths and values of the valence angles in exocycle H(23)-C(3)-C(6)-C(9)-C(14)-C(15)-H(26) change.

Similar type of intramolecular interaction, leading to torsion of a molecule into a spiral with preservation of standard values of interatomic spacing intervals and valence angles, can be seen in the benzophenanthrene molecule (Figure 6) [8]. Probably in cation **C** the energy of conjugating would be so great, that it does not allow the structure to bend in a spiral to decrease sterical tension. Obviously the inability of the molecule to undergo removal of intramolecular strain is the main reason why it can not be synthesized.

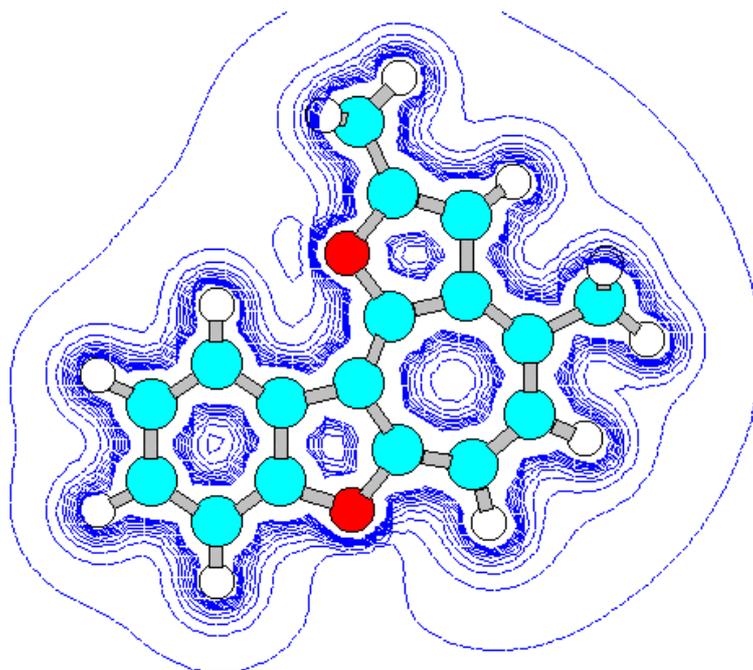


Figure 2. Energy minimized structure (AM1) of cation **B** generated by HyperChem 5.0 program (with 2Dcontour map of electrostatic potential).

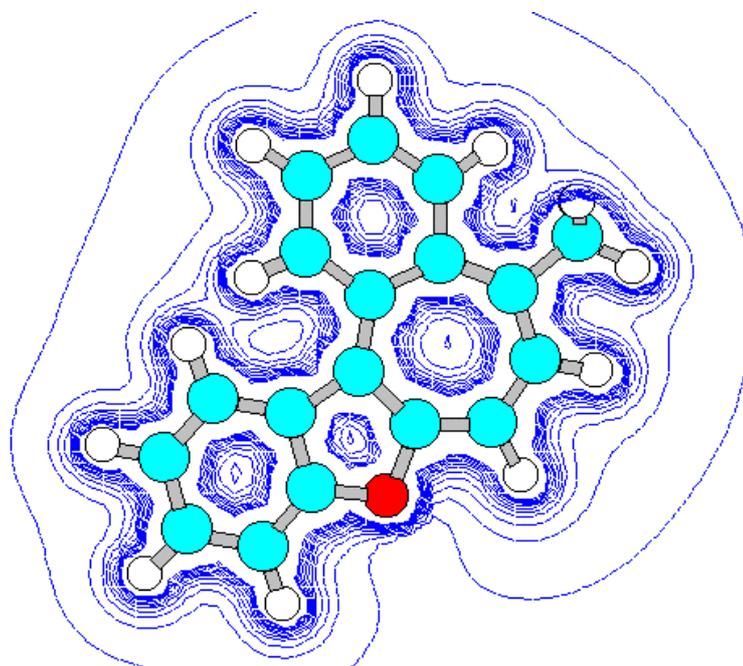


Figure 3. Energy minimized structure (AM1) of hypotetic cation **C** generated by HyperChem 5.0 program (with 2Dcontour map of electrostatic potential).

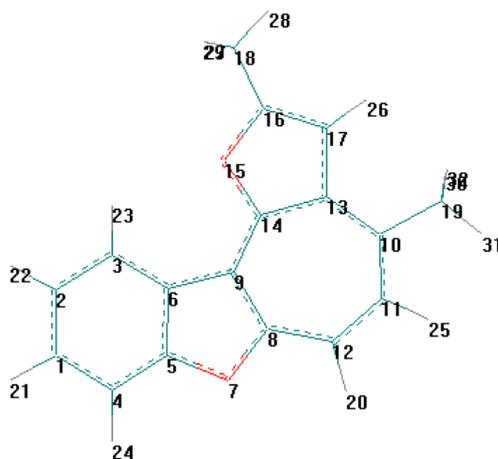


Figure 4.

Table 8. Bond lengths (Å) for compound B from X-ray and AM1 data.*

C(1) - C(2)	1.400 (5)	1.403	C(2) - C(3)	1.368 (5)	1.394
C(3) - C(6)	1.412 (5)	1.394	C(5) - C(6)	1.391 (5)	1.430
C(4) - C(5)	1.387 (5)	1.387	C(1) - C(4)	1.387 (5)	1.398
C(5) - O(7)	1.374 (4)	1.404	O(7) - C(8)	1.375 (4)	1.401
C(8) - C(9)	1.411 (5)	1.434	C(6) - C(9)	1.446 (5)	1.448
C(8) - C(12)	1.382 (5)	1.390	C(11) - C(12)	1.385 (5)	1.385
C(10) - C(11)	1.399 (5)	1.399	C(10) - C(13)	1.411 (5)	1.397
C(13) - C(14)	1.406 (5)	1.436	C(9) - C(14)	1.377 (5)	1.383
C(10) - C(19)	1.513 (5)	1.490	O(15) - C(14)	1.358 (4)	1.394
O(15) - C(16)	1.382 (4)	1.410	C(16) - C(17)	1.339 (5)	1.377
C(13) - C(17)	1.430 (5)	1.455	C(16) - C(18)	1.481 (5)	1.463

*Bold numbers are quantum semi-empirical AM1 calculation data

Table 9. Bond angles (deg) for compound B from X-ray and AM1 data.*

C(1) - C(2) - C(3)	122.3 (3)	121.7	C(2) - C(3) - C(6)	116.9 (3)	118.0
C(3) - C(6) - C(5)	119.9 (3)	119.2	C(4) - C(5) - C(6)	123.5 (3)	123.3
C(1) - C(4) - C(5)	115.6 (3)	116.0	C(2) - C(1) - C(4)	121.8 (3)	121.8
C(5) - O(7) - C(8)	106.9 (3)	106.4	O(7) - C(8) - C(9)	110.1 (3)	110.4
C(6) - C(9) - C(8)	106.0 (3)	106.4	C(5) - C(6) - C(9)	105.6 (3)	106.0
C(6) - C(5) - O(7)	111.5 (3)	110.8	C(8) - C(12) - C(11)	127.5 (3)	127.2
C(10) - C(11) - C(12)	131.2 (3)	130.8	C(11) - C(10) - C(13)	125.4 (3)	126.3
C(10) - C(13) - C(14)	127.9 (3)	129.1	C(9) - C(14) - C(13)	132.8 (3)	130.9
C(8) - C(9) - C(14)	123.7 (3)	123.6	C(9) - C(8) - C(12)	131.4 (3)	132.1
C(11) - C(10) - C(19)	116.8 (3)	117.1	C(14) - O(15) - C(16)	107.0 (3)	107.1
O(15) - C(16) - C(17)	110.6 (3)	110.4	C(13) - C(17) - C(16)	107.7 (3)	107.7
C(14) - C(13) - C(17)	105.0 (3)	105.4	C(13) - C(14) - O(15)	109.7 (3)	109.5

*Bold numbers are quantum semi-empirical AM1 calculation data

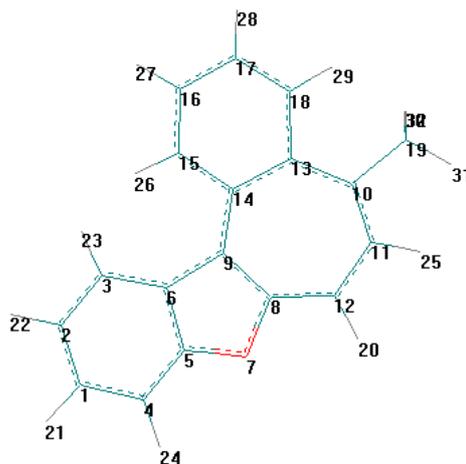


Figure 5.

Table 10. Bond lengths (Å) for C from AM1 data.

C(1) - C(2)	1.403	C(2) - C(3)	1.391
C(3) - C(6)	1.404	C(5) - C(6)	1.435
C(4) - C(5)	1.391	C(1) - C(4)	1.391
C(5) - O(7)	1.389	O(7) - C(8)	1.406
C(8) - C(9)	1.429	C(6) - C(9)	1.466
C(8) - C(12)	1.384	C(11) - C(12)	1.380
C(10) - C(11)	1.389	C(10) - C(13)	1.431
C(13) - C(14)	1.438	C(9) - C(14)	1.425
C(10) - C(19)	1.499	C(14) - C(15)	1.429
C(15) - C(16)	1.372	C(16) - C(17)	1.407
C(17) - C(18)	1.372	C(13) - C(18)	1.436
C(3) - H(23)	1.098	C(15) - H(26)	1.095
H(23) ... H(26)	1.628		

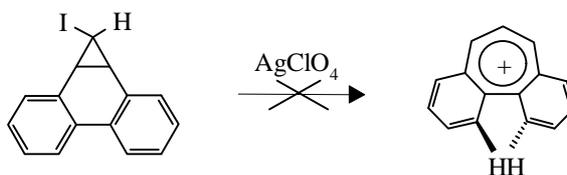
Table 11. Bond angles (deg). For C from AM1 calculation data.

C(1) - C(2) - C(3)	122.4	C(2) - C(3) - C(6)	119.9
C(3) - C(6) - C(5)	115.5	C(4) - C(5) - C(6)	125.6
C(1) - C(4) - C(5)	116.3	C(2) - C(1) - C(4)	120.4
C(5) - O(7) - C(8)	106.0	O(7) - C(8) - C(9)	111.7
C(6) - C(9) - C(8)	104.9	C(5) - C(6) - C(9)	106.1
C(6) - C(5) - O(7)	111.2	C(8) - C(12) - C(11)	125.6
C(10) - C(11) - C(12)	129.9	C(11) - C(10) - C(13)	129.2
C(10) - C(13) - C(14)	128.6	C(9) - C(14) - C(13)	127.0
C(8) - C(9) - C(14)	125.2	C(9) - C(8) - C(12)	134.4
C(11) - C(10) - C(19)	112.7	C(14) - C(15) - C(16)	124.1
C(15) - C(16) - C(17)	119.0	C(16) - C(17) - C(18)	119.0
C(13) - C(18) - C(17)	123.9	C(13) - C(14) - C(15)	117.0
C(14) - C(15) - H(26)	119.2	C(6) - C(3) - H(23)	123.8



Figure 6.

This example is not the only one known. It is of interest that the dibenzo[a,c]tropylium cation was not obtained by the route shown in Scheme 5 due to steric hindrance caused by two overlapping hydrogens which makes complanarity of the aromatic cation impossible (Scheme 5) [9]:



Scheme 5.

Instead a green polymer was isolated despite the high stability of the cation predicted by MO LCAO. However dibenzo[a,d]tropylium salts are stable compounds[10].

Experimental

General

^1H NMR spectra were registered on Tesla BS-587 (80 MHz) in CDCl_3 , with hexamethyldisiloxane as internal standard. IR spectra were obtained on Specord M80 in vaseline. The course of a reaction was controlled by TLC on Sorbfil plates (bromine and dinitrophenylhydrazine solution as a developer).

General method of synthesis of 2-hydroxybenzyl alcohols 1

To a Grignard reagent prepared from 0.25 mol of the corresponding halide and 6.8 g (0.28 mol) of Mg in 250 ml of dry ether 13.6 g (0.1 mol) of substituted salicylaldehyde was added dropwise. The mixture was stirred for 5 minutes and then decomposed by slow addition of water until magnesium salts coagulated. The ether layer was separated and the solid residue in the flask repeatedly extracted with ether, combined extracts were dried over Na_2SO_4 and evaporated. The oily residue was dissolved in a hot benzene-hexane mixture, filtered through a pad of Al_2O_3 and left to crystallize overnight.

1a Yield 73%. M. p. 102-103°C. Analysis: Found C, 78.31; H 6.25; $\text{C}_{14}\text{H}_{14}\text{O}_2$, M_r 214.26 requires C, 78.48; H 6.58. ^1H NMR δ 2.13 (s, 3H, CH_3), 2.91 (b. s, 1H, CHOH), 5.87 (b. s, 1H, CH), 6.61-6.86

(m, 3H, H_{Ar}), 7.29 (s, 5H, H_{Ar}), and 7.60 (b. s, 1H, OH). IR 3190 (b. s, OH) and 3530 cm⁻¹ (s, OH).

1b Yield 72%. M. p. 106-107°C. Analysis: Found C, 57.01; H 4.79; C₁₄H₁₃BrO₂, M_r 293.16 requires C, 57.36; H 4.47. ¹H NMR δ 2.14 (s, 3H, CH₃), 3.17 (b. s, 1H, CHOH), 5.78 (s, 1H, CH), 6.61-6.86 (m, 3H, H_{Ar}), 7.17 (d, J = 8.2 Hz, 2H, H_{Ar}), 7.30 (d, J = 8.2 Hz, 2H, H_{Ar}) and 7.62 (s, 1H, OH). IR 3210 (b. s, OH) and 3520 cm⁻¹ (s, OH).

1c Yield 81%. M. p. 97-98°C. Analysis: Found C, 79.11; H 7.25; C₁₅H₁₆O₂, M_r 228.29 requires C, 78.92; H 7.06. ¹H NMR δ 2.12 (s, 3H, CH₃), 2.26 (s, 3H, CH₃), 3.02 (b. s, 1H, CHOH), 5.79 (b. s, 1H, CH), 6.58-6.82 (m, 3H, H_{Ar}), 7.13 (s, 4H, H_{Ar}) and 7.73 (s, 1H, OH). IR 3310 cm⁻¹ (b. s, OH).

1d Yield 78%. M. p. 87-88°C. Analysis: Found C, 78.16; H 5.89; C₁₃H₁₂O₂, M_r 200.23 requires C, 77.98; H 6.04. ¹H NMR 2.99 (b. s, 1H, CHOH), 5.92 (b. s, 1H, CH), 6.69-7.40 (m, 9H, H_{Ar}) and 7.83 (b. s, 1H, OH). IR 3215 (b. s, OH) and 3520 cm⁻¹ (s, OH).

1e Yield 73%. M. p. 104-105°C. Analysis: Found C, 78.24; H 6.89; C₁₄H₁₄O₂, M_r 214.26 requires C, 78.48; H 6.58. ¹H NMR δ 2.25 (s, 3H, CH₃), 3.07 (b. s, 1H, CHOH), 5.84 (s, 1H, CH), 6.64-7.30 (m, 8H, H_{Ar}) and 7.95 (b. s, 1H, OH). IR 3205 (b. s, OH) and 3530 cm⁻¹ (s, OH).

1f Yield 69%. M. p. 82-83°C. Analysis: Found C, 78.59; H 6.72; C₁₅H₁₆O₂, M_r 228.29 requires C, 78.92; H 7.06. ¹H NMR δ 2.16 (s, 3H, CH₃), 2.57 (b. s, 1H, CHOH), 3.01 (d, J = 7.0 Hz, 2H, CH₂), 4.87 (t, J = 7.0 Hz, 1H, CH), 6.61-6.82 (m, 3H, H_{Ar}), 7.20 (s, 5H, H_{Ar}), and 7.70 (b. s, 1H, OH). IR 3170 (b. s, OH) and 3480 cm⁻¹ (s, OH).

1g Yield 53%. M. p. 142-143°C. Analysis: Found C, 71.89; H 4.78; C₁₀H₁₄O₂, M_r 166.22 requires C, 72.26; H 4.49. ¹H NMR δ 0.72 (t, J = 7.2 Hz, 3H, CH₂CH₃), 1.84 (k. d, 2.16 J = 7.2 Hz, J = 7.1 Hz, CH₂CH₃) 2.17 (s, 3H, CH₃), 4.23 (t, J = 7.1 Hz, 1H, CH), 6.55-6.87 (m, 3H, H_{Ar}), and 7.08 (s, 1H, OH). IR 3190 (b. s, OH) and 3370 cm⁻¹ (s, OH).

General method of synthesis of 2-hydroxyaryl-R - (5-methylfur-2-yl)methanes **2**

The mixture of 0.02 mol of alcohol **1**, 0.022 mol of 2-methylfuran and 50 mg of *p*-toluenesulphonic acid in 20 ml of benzene was refluxed with Dean-Stark trap for 5 minutes. Cooled solution was filtered through a pad of Al₂O₃ and evaporated to dryness, leaving a product as a colourless oil.

General method of synthesis of 3-R-2 - (3-oxobutyl)benzo[b]furans **3**

To a boiling solution of 0.01 mol of compound **2** in 5 ml of ethanol, 5 ml of saturated ethanolic HCl was added all at once. The reaction mixture was refluxed for 5 minutes, then cooled, diluted with water. The thick oil was washed with water and extracted with hot hexane. The warm extract was filtered through a pad of Al₂O₃, the mother liquor concentrated and left to crystallize at -5°C to give product as white crystals.

References and Notes

1. Butin, A. V.; Stroganova T. A.; Abaev, V. T.; Kul'nevich, V. G. *Khim. Geterotsikl. Soedin.* **1998**, 1250.
2. Gutnov, A. V.; Abaev, V. T.; Butin, A. V.; Zavodnik, V. E.; Kul'nevich, V. G. *Khim. Geterotsikl. Soedin.* **1996**, 162.
3. Abaev, V. T.; Gutnov, A. V.; Butin, A. V. *Khim. Geterotsikl. Soedin.* **1998**, 603.
4. Butin, A. V.; Abaev, V. T.; Zavodnik, V. E.; Kul'nevich, V. G. *Khim. Geterotsikl. Soedin.* **1993**, 627.
5. Butin, A. V.; Gutnov, A. V.; T. A. Abaev, V. T.; Krapivin, G. D. *Khim. Geterotsikl. Soedin.* **1998**, 883.
6. Butin, A. V.; Gutnov, A. V.; T. A. Abaev, V. T.; Krapivin, G. D. *Molecules* **1999**, 52.
7. Butin, A. V.; Krapivin, G. D.; Zavodnik, V. E.; Kul'nevich, V. G. *Khim. Geterotsikl. Soedin.* **1993**, 616.
8. Herbstein, F.N., Schmidt, G.M.J. *J. Chem. Soc.*, **1954**, 3302
9. Dewar, M. J. S.; Ganellin, C.R. *J.Chem. Soc.* **1959**, 3139.
10. Berti, G.; Da Settimo A. *Ann. Chimica* **1962**, 995.

Samples Availability: Available from MDPI.

© 1999 by the authors. Reproduction of this article, by any means, is permitted for noncommercial purposes.