Synthesis and One-Electron Oxidation Chemistry of Stable β,β-Dimesityl Enols with Heteroaryl Substituents

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Four novel stable enols (one characterized by X-ray crystal structure analysis) were synthesized and investigated under oxidative conditions to yield benzofurans. Depending on the donor qualities of the heteroaryl substituent the reaction following the one-electron oxidation could be stopped on the stage of the cyclohexadienyl cation whose lifetime was measured. Oxidation potentials were determined for the enols, the enolates and the α-carbonyl radicals. Oxidation of benzofurans yielded dimeric species or intramolecular cyclization products.

Key words: Stable Conjugated Enols, One-Electron Oxidation, Radical Cations, Benzofurans, Cyclic Voltammetry

Introduction

The reactivity of enol and enol ether radical cations [1, 2] is being extensively investigated due to their pivotal role played in DNA damage [3], in important biological transformations [4] carried out by coenzyme B_{12} dependent enzymes (such as diol dehydratase), and in Ribonucleotide Reductase [5]. While enol ether radical cations can readily be prepared from their neutral precursors, such a simple oxidative strategy is precluded for enols as these constitute mostly fleetingly existing tautomers of carbonyl compounds. The last 20 years, however, have witnessed a steadily increasing knowledge about the synthesis and structures of isolable enols [6 – 8] which paved the way for direct studies on the reactivity patterns of enol radical cations in solution [9 – 11]. As the primary reaction of enol radical cations, both in solution and in the enzyme, should be controlled by the competition of deprotonation *vs.* electron transfer, the importance of hydrogen bonding on both the deprotonation rate constant and the redox potential (oxidation potentials are lowered by more than 500 mV) [12] is crucial. After deprotonation the resultant α-carbonyl radical is further oxidized to the α-carbonyl cation [13], the fate of which has been investigated only rarely. The present study seeks to shed light on the role of good donor substituents, such as thiophene, and furan, on the redox potential data of heteroaryl substituted enols and on the reactivity of intermediates involved in the oxidation.

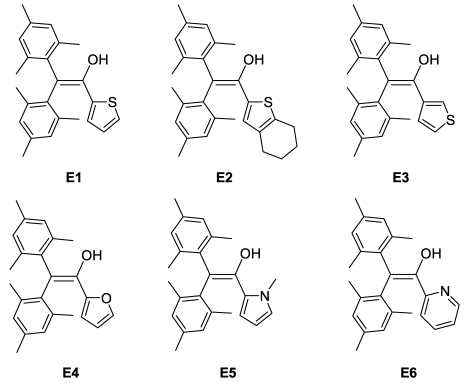

Chart 1.

The one electron oxidation chemistry of aryl or alkyl enols has been extensively studied [9 – 11]. A working model has been proposed and is as follows: enol radical

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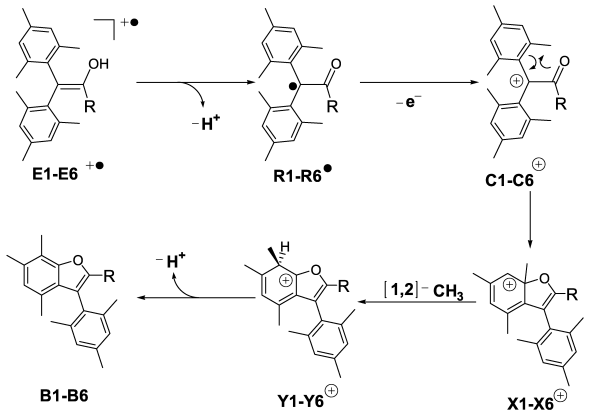

Scheme 1. Schematic representation of the mechanism of benzofuran formation upon oxidation of stable enols [9 – 11].

cation $\mathbf{E}^{\bullet+}$ formed after one-electron oxidation undergoes a fast deprotonation leading to the sterically encumbered α-carbonyl radical $\mathbf{R}^{\bullet}$. This α-carbonyl radical is further oxidized to α-carbonyl cation $\mathbf{C}^{+}$ which undergoes a fast Nazarov type cyclization to form the cation $\mathbf{X}^{+}$. Benzofuran derivative are finally formed after a fast 1,2-methyl shift followed by deprotonation. The present investigation will demonstrate that with R = heteroaryl donor a significant retardation of the $\mathbf{X}^{+} \rightarrow \mathbf{Y}^{+}$ rearrangement occurs while it is rapid with a heterocyclic acceptor substituent.

Results and Discussion

Synthesis

β,β-Dimesityl enols **E1 – E4** were synthesized according to an approach introduced by Fuson *et al.* [14] and also used by Rappoport *et al.* [15] that had earlier been used successfully for the preparation of **E6** [12]. Accordingly, dimesityl ketene [16], prepared from dimesitylacetic acid, was reacted with appropriate Grignard or lithium reagents. The enols **E1 – E4** were obtained in tautomerically pure form after column chromatography or recrystallization.

Attempts to synthesize **E5** were unsuccessful; instead the tautomeric ketone **K5** was isolated in 7% yield besides **E7** and a plethora of unidentified mostly polymeric products.

Characterization

The structure of the enols was established based on their spectral data (IR, ^{1}H NMR, ^{13}C NMR and elemental analysis). The infra-red spectra (recorded in KBr) of enols **E1 – E4** exhibited sharp O-H absorption bands just below 3500 cm^{-1} while for ketone **K5** no O-H absorption was observed but instead a C=O absorption at 1644 cm^{-1}. Such a shift to lower wave number is indicative of a strong conjugation between the carbonyl group and the *N*-methyl pyrrole.

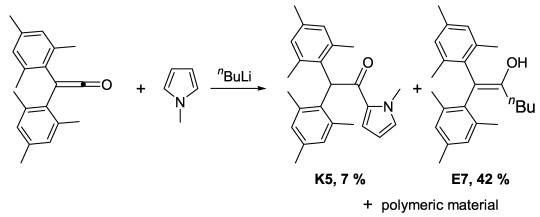

Chart 2.

A sharp OH signal was observed in ^{1}H NMR spectra of enols **E1 – E4** between 5.01 and 5.12 ppm, while the mesityl rings in all four β,β-dimesityl enols showed coalescence phenomena due to the hindered rotation which is a common feature of these enols [17]. However in **K5**, no such coalescence was registered for the mesityl groups. The methine proton was observed at 6.08 ppm being slightly shifted upfield compared to the usual range (6.11 to 6.13 ppm) for such ketones. A ^{13}C NMR signal at 192.4 ppm for the C=O signal confirms the tautomerization of enol **E5** to **K5** and equally highlights the strong conjugative effect of the pyrrole ring.

X-ray crystal structure analyses

For **E2** and **K5** crystals suitable for X-ray analysis were obtained. Some of the bond distances, angles and torsional angles of **E2** (Table 1, Table 2) and **K5** (Table 3) are tabulated below. The data will be compared with those of other solid state structures of enols [18 – 20].

It is apparent that **E2** exists as enol both in solid (Fig. 1a) as well as in solution. The solid state structure reveals that the length of the double bond between C(1) and C(2) is remarkably longer (*i.e.* 3.0 pm) than for the phenyl [20] or anthryl substitued enol [18].

The dihedral angles between C(1)-C(2)-C(21)-C(26), C(1)-C(2)-C(11)-C(12) and C(2)-C(1)-C(31)-C(32) indicate that both mesityl rings and the tetrahydrobenzothienyl group are twisted out of the plane of the double bond. The C(2)-C(1)-C(31)-C(32) angle (23.7°) is smaller than in enols with phenyl (33.3°) or anthryl substitution (62.5°). A reason for the small torsion angle may be the much stronger overlap of the

Table 1. Some important bond lengths [pm] and angles [°] in enol **E2**.

C(1)-O	134.9 (5)	C(31)-C(32)	144.5 (7)
C(1)-C(2)	136.9 (5)	C(32)-C(33)	144.9 (6)
C(1)-C(31)	146.6 (5)	C(33)-C(34)	135.7 (6)
C(1)-C(2)-C(11)	119.6 (3)	C(2)-C(1)-C(31)	126.7 (3)
C(11)-C(2)-C(21)	121.0 (3)	C(2)-C(31)-C(32)	125.6 (3)
C(1)-C(2)-C(21)	119.1 (3)	C(31)-C(32)-C(33)	108.5 (5)
O-C(1)-C(2)	119.0 (3)	C(32)-C(33)-C(34)	113.7 (4)
O-C(1)-C(31)	114.2 (3)		

Table 2. Some important torsional angles [°] in **E2**.

O-C(1)-C(2)-C(21)	11.1 (5)
C(1)-C(2)-C(21)-C(26)	60.1 (5)
C(2)-C(1)-C(31)-C(32)	−156.3 (4)
C(31)-C(32)-C(33)-C(34)	−0.8 (5)
C(1)-C(2)-C(11)-C(12)	53.6 (5)

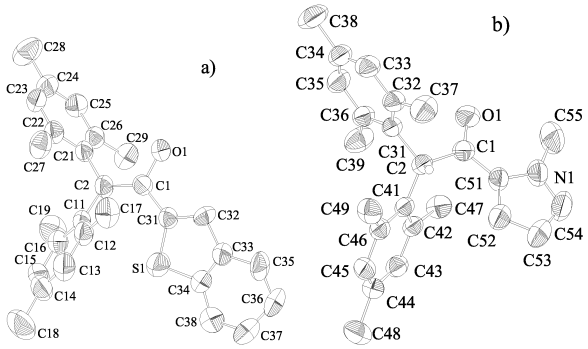

Fig. 1. ORTEP drawings of a) enol **E2**, and b) ketone **K5**.

tetrahydrobenzothienyl moiety with the double bond that is reflected by a rather short distance (146.6 pm) between C(1)-C(31). The *anti* conformation for the OH group was established by the riding method [21, 22].

The crystal structure of **K5** (Fig. 1b) confirms that **E5** was received as a ketone tautomer (in agreement with other spectroscopic data in solution) with a length of 153.4 pm for the C(1)-C(2) bond. A strong conjugation between the pyrrole ring and the carbonyl group is apparent from the dihedral angle O1-C(1)-C(51)-N1 (4.1°) and a short single bond C(1)-C(51) (145.9 pm), in particular when compared with the bonds C(2)-C(31) and C(2)-C(41) (153.7 and 153.8 pm). The C(1)-C(51) bond was also found to be shorter than in phenyl-substituted 2,2-dimesitylethanone (152.1 pm) [20].

Preparative scale oxidation

Preparative scale one-electron oxidations of the enols **E1 – E4, E6** were performed by addition of copper(II) triflate ($Cu(OTf)_2$, $E_{1/2} = 0.67$ V_{Fc}) or nitrosonium hexafluoroantimonate ($NOSbF_6$, $E_{pa} = 0.79$ V_{Fc}). The preparative oxidation of most of the donor substituted enols **E1 – E5** led to polymerized products, with only the benzofuran **B1** being isolated from **E1** in yields up to 68% after 3 h. In contrast, oxidation of **E6** with $NOSbF_6$ smoothly provided benzofuran **B6** in 73% yield after 1 min.

Table 3. Some important bond angles [°] observed for **K5** in solid state.

C(2)-C(1)-O	121.1 (2)	O-C(1)-C(51)	122.4 (2)
C(2)-C(1)-C(51)	116.4 (2)		

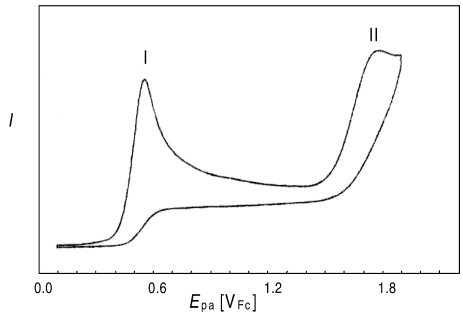

Fig. 2. Representative cyclic voltammogram of enols, here shown with **E1**, in acetonitrile at 100 mV s^{-1}.

Cyclic voltammetry investigations

Cyclic voltammetry investigation of enols **E1 – E4** exhibited an irreversible oxidation wave at $E_{pa} = 0.46 – 0.58$ V_{Fc} at 100 mV s^{-1} in acetonitrile. The irreversibility of the oxidation signal suggests a rapid follow-up reaction of the enol radical cation which is most likely deprotonation [10]. No reversible or partially reversible wave for the benzofuran derivative was detected during the cyclic voltammograms of **E1 – E4** as seen for aryl/alkyl enols [9]. Instead, in addition to the first wave assigned to the oxidation of enols **E1 – E4** an irreversible oxidation wave at rather high anodic potential ($\Delta E_{pa} = 0.9 – 1.3$ V) was found. Recent investigations [23] propose that the second wave can be assigned to the oxidation of the cyclohexadienyl cations $\mathbf{X}^+$ which are persistent intermediates in the oxidative transformation of electron-rich enols.

The cyclic voltammogram (cv) of ketone **K5** exhibited an irreversible oxidation wave at $E_{pa} = 1.48$ V_{Fc} which is consistent with comparable substrates [9].

Enols **E1 – E4** were transformed to the corresponding enolates **A1 – A4** by addition of tetramethylam-

Table 4. Oxidation potentials of the enols by cyclic voltammetry at 100 mV s^{-1} in acetonitrile.

System	E_{pa} (**E**) [V_{Fc}]	$E_{1/2}$ (**A**) [V_{Fc}]	E_{pa} ($\mathbf{R}^{\bullet}$) [V_{Fc}]	E_{pa} ($\mathbf{X}^{+}$) [V_{Fc}]
1	0.53	−0.78	0.24	1.80
2	0.46	−0.77	0.27	1.64
3	0.58	−0.99	nd	1.89
4	0.50	−0.78	0.27	1.79

monium hydroxide (1 equiv.). The cv's of **A1 – A4** exhibited two waves in the oxidative scan, the first wave of which was reversible and was assigned to reversible oxidation of the enolate to the α-carbonyl radical $\mathbf{R}^{\bullet}$ (persistent). In contrast, the second wave corresponding to the oxidation of the radical $\mathbf{R}^{\bullet}$ to the α-carbonyl cation $\mathbf{C}^{+}$ (Table 4) was irreversible indicative of a fast follow-up reaction of $\mathbf{C}^{+}$. The oxidation potentials of $\mathbf{X}^{+}$ show a reduced electron-donating effect of the 3-thienyl group with respect to the other heteroaryl substituents that is also visible with enols **E**.

UV/vis kinetic investigations

Both, the reactions with $Cu(OTf)_2$ and the cyclic voltammetric investigations revealed a intensely red colored species upon oxidation of enols **E1 – E4** or oxidation of the enolates **A1 – A4**. The UV/vis investigations showed a persistent species with $\lambda_{max} = 501$ to 512 nm, which through analogy to electron-rich aryl systems [23] and NMR could be assigned as cation $\mathbf{X}^{+}$, for which the [1,2]-methyl shift constitutes the rate determining step. ^{1}H NMR investigations showed typical signals both in the aromatic (7.50 pppm) and aliphatic region (1.96 – 1.98 ppm) in line with ^{1}H NMR on $\mathbf{X}^{+}$ with R = 3,4-dimethoxyphenyl [23]. The [1,2]-methyl shift is significantly slowed down by electron donating substituents in α-position [24], such as the 3,4-dimethoxyphenyl substituent, with $k\,(\mathbf{X}^{+} \rightarrow \mathbf{Y}^{+}) = 2.28 \cdot 10^{-2}$ min^{-1} ($t_{1/2}$ = 30.4 min) [23]. In all spectra, the formation of an isobestic point indicated the clean interconversion of the cation $\mathbf{X}^{+}$ to **B**, as the increasing wave at $\lambda_{max} = 312 – 327$ nm can be assigned to the benzofurans. This could be verified from the UV/vis spectrum of pure **B1** exhibiting $\lambda_{max} = 327$ nm. The problems to obtain benzofurans **B** (except for **B1**) from preparative oxidation must hence be a consequence of rapid follow-up reactions (apparently polymerization) of **B** under oxidative conditions.

The kinetic decay of cations $\mathbf{X}^{+}$ was monitored at 501 – 512 nm at room temp. and followed a first-order decay. The decay of $\mathbf{X3}^{+}$ proved to be more rapid than that of $\mathbf{X1}^{+}$ in line with higher oxidation potential of $\mathbf{X3}^{+}$ (this indicates a reduced stabilization of the cation) and the tendency of thiophene to undergo electrophilic substitution in position 2 over 3.

Table 5. Absorption, half-life and rate constant for cations X^{+} at room temp.

Cation	λ_{max} [nm]	$t_{1/2}$ [min]	k [10^{-2} min^{-1}]
$\mathbf{X1}^{+}$	512	18.4	3.78
$\mathbf{X3}^{+}$	501	7.2	9.60
$\mathbf{X4}^{+}$	509	17.3	4.00

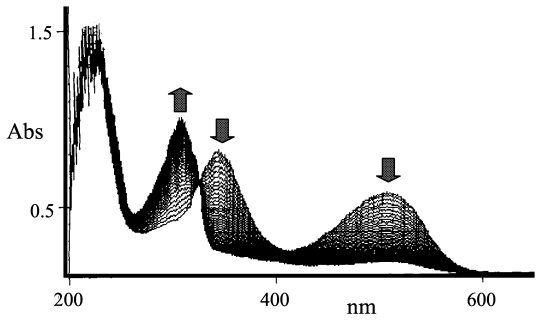

Fig. 3. UV/vis spectrum of the decay of $\mathbf{X3}^{+}$ obtained by oxidizing **E3** with copper(II) triflate.

In contrast, the rapid oxidative formation of **B6** within 1 min illustrates that an acceptor heterocyclic substituent triggers a rapid rearrangement of $\mathbf{X}^{+}$ to finally afford the benzofuran.

*Oxidation of benzofuran **B1,B6***

In contrast to our earlier observations [11] that C-2 substituted benzofurans exhibit reversible oxidation waves in cyclic voltammetry studies, only a partially reversible wave was observed for **B1** at $E_{1/2} = 0.68$ V_{Fc}. In addition to the oxidation wave, a reduction wave at $E_{pc} = 0.45$ V_{Fc} was observed which could not arise from reduction of $\mathbf{B1}^{\bullet+}$ and hence must derive from a follow up product. Preparative scale oxidation of the benzofuran **B1** with one equivalent of copper(II) triflate furnished the isolated dimer **BT1** in 90% yield. Electrochemical oxidation of this product indeed revealed a potential of 0.45 V_{Fc}, thus indicating that **BT1** is the follow up oxidation product of **B1** in the cyclic voltammetry investigation.

The mechanism for this dimerization is similar to the electrocoupling reactions of aromatic compounds and thiophenes [25 – 27]. Thus the bithiophene derivative **BT1** is formed by dimerization of the thiophene

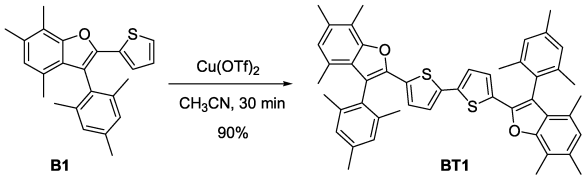

Chart 3.

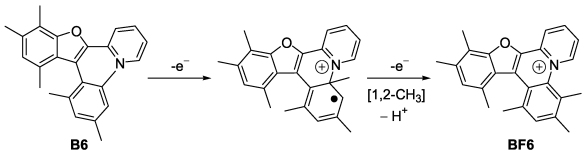

Chart 4.

type radical cations $\mathbf{B1}^{\bullet+}$ followed by double deprotonation.

As for **B1** the cyclic voltammetric investigation of **B6** revealed an irreversible oxidation wave ($E_{pa} = 0.99$ V_{Fc}) indicative of a fast follow-up reaction. At higher potential an additional wave was recorded that at scan rates > 100 mV s^{-1} became reversible ($E_{1/2} = 1.35$ V_{Fc}). In presence of trifluoroacetic acid the first wave disappeared, providing a new irreversible wave at $E_{pa} = 1.29$ V_{Fc} while the wave at $E_{1/2} = 1.35$ V_{Fc} remained undisturbed. In presence of 2,6-di-*tert*-butylpyridine both waves remained unaffected. These results are consistent with the following mechanistic hypothesis: upon one-electron oxidation of **B6** a distonic radical cation is formed that after a second one-electron oxidation undergoes a 1,2-methyl shift followed by deprotonation. The resultant **BF6** is further oxidized at $E_{1/2} = 1.35$ V_{Fc}.

Conclusion

The presence of a five-membered heteroaromatic ring not only affects the oxidation potentials of enols, but also the follow-up processes of these enols. The electron donating ability of the five-membered heterocycles (containing oxygen and sulfur) lowers the oxidation potential and also stabilizes the $\mathbf{X}^+$ to such an extent that other follow up reactions may predominate leading to polymerization rather than to benzofuran formation.

Experimental Section

Reagents were purchased from standard chemical suppliers and were used without further purification. Dimesitylketene was prepared as described in the literature [16].

Table 6. Data for the X-ray crystal structure determination of **E2** and **K5**.

Compound	**E2**	**K5**
Empirical formula	$C_{28}H_{32}OS$	$C_{25}H_{29}NO$
Formula weight	416.60	359.49
Temperature	293(2) K	293(2) K
Wavelength	0.70930 Å	0.70930 Å
Crystal system	orthorhombic	orthorhombic
Space group	*Pcab* (No. 61)	*Pcab* (No. 61)
Unit cell dimensions [Å]	$a = 8.809(2)$,	$a = 11.431(2)$,
	$b = 17.664(4)$,	$b = 15.469(6)$,
	$c = 30.579(6)$,	$c = 23.463(4)$,
Volume	4758(2) $Å^3$	4148.9(18) $Å^3$
Z	8	8
Density (calculated)	1.163 mg/mm^3	1.151 mg/mm^3
Absorption coefficient	0.152 mm^{-1}	0.069 mm^{-1}
$F(000)$	1792	1552
Crystal size [mm^3]	$0.8 \times 0.6 \times 0.3$	$0.6 \times 0.5 \times 0.5$
Θ range for data collection	2.30 to 22.94°	2.37 to 20.93°
Index ranges	$0 \le h \le 9$,	$0 \le h \le 11$,
	$0 \le k \le 19$,	$0 \le k \le 15$,
	$0 \le l \le 33$	$0 \le l \le 23$
Reflections collected	3296	2222
Independent reflections	3296	2222
R(int)	0.0000	0.0000
Refinement	Full-matrix least-squares on F^2	
Absorption correction		Psi-scans
Max. and min. transmission		0.9983 and 0.8989
Data/restraints/parameters	3295 / 24 / 321	2215 / 0 / 252
Goodness-of-fit on F^2	1.041	1.077
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0679$,	$R1 = 0.0382$,
	$wR2 = 0.1963$	$wR2 = 0.0988$
R indices (all data)	$R1 = 0.0876$,	$R1 = 0.0450$,
	$wR2 = 0.2214$	$wR2 = 0.1450$
Largest diff. peak	0.680	0.134
and hole [$eÅ^{-3}$]	and −0.446	and −0.118

Acetonitrile used for the cyclic voltammetry investigations and the one-electron oxidation reactions was of HPLC quality (Riedel-de Haen) and distilled from CaH_2.

Melting points were recorded with a Büchi Smp-20 apparatus. Infrared Spectra: Perkin-Elmer 1605 FT-IR infrared spectrophotometer. ^{1}H NMR spectra: Bruker AC 200 (200 MHz), Bruker AC 250 (250 MHz), tetramethylsilane as internal standard; ^{13}C NMR: Bruker AC 200 (50 MHz), [D]chloroform and tetramethylsilane as internal standard. Mass spectra: MAT 90, Finnigan; MAT 8200, Finnigan. Combustion analyses for elemental composition were performed by the Analytical Division of the Institute of Inorganic Chemistry, University of Würzburg (Carlo Erba 1106).

Cyclic voltammetry experiments: The cyclic voltammetry experiments were performed with a potentiostat Model 362 (Princeton Applied Research) and recorded using an x,y,t recorder Modell PM 8271 (Philips). The electrochemical cell was equipped with a platinum disc (1.0 mm diameter) working electrode, a platinum auxiliary electrode and a silver wire as reference electrode. The measurements were taken at 5 –

10 mM concentration and ferrocene (Fc) was used as internal reference (0.39 V *vs.* SCE).

*2,2-Dimesityl-1-(2-thienyl)ethenol (***E1***)*

n-Butyllithium (7.44 ml, 1.60 M in THF, 11.9 mmol) was added dropwise to an ice-cold solution of thiophene (940 μl, 1.00 g, 11.9 mmol) in 40 ml of dry THF. The solution was stirred at 0 °C for 15 min, then at r.t. for 30 min. A solution of dimesityl ketene (3.31 g, 11.9 mmol) in dry THF (20 ml) was added to the reaction mixture and stirred for 5 h at r.t. The reaction was quenched with NH_4Cl (sat. aq., 30 ml) solution, extracted with Et_2O (3×20 ml), dried over Na_2SO_4 (anhyd.) and concentrated. The crude product was purified by column chromatography with cyclohexane/ethyl acetate, 3:1 as eluent yielding a partially pure solid which was recrystallized from ethanol (2.30 g, 6.34 mmol, 53%). **E1**: Mp 152 – 155°C. – IR (KBr): $\tilde{\nu} = 3487$ (s, OH), 2916 (s, CH), 1608 (s), 1585 (s), 1555 (m), 1438 (s), 1374 (s), 1264 (m), 1210 (s) 1160 (s), 1012 (s), 896 (s), 855 (s) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 250 MHz,): $\delta = 1.99$, 2.17, 2.25, 2.27 (coalescence, 18 H, Mes-CH_3), 5.12 (s, 1 H, OH), 6.76 (s, 2 H, Mes-H), 6.85 (dd, 1 H, $J = 3.8$, 5.0 Hz, 4'-H), 6.90 (s, 2 H, Mes-H), 6.93 (dd, 1 H, $J = 1.2$, 3.8 Hz, 3'-H), 7.16 (dd, 1 H, $J = 1.2$, 5.0 Hz, 5'-H). – ^{13}C NMR ($CDCl_3$, 63 MHz) $\delta = 20.73$, 20.81, 20.87, 20.91, 111.50, 126.29, 126.55, 127.52, 129.42, 129.93, 130.21, 132.21, 134.60, 136.47, 136.98, 138.41, 138.77, 139.21, 144.87. – $C_{24}H_{26}OS$ (362.52): calcd. C 79.51, H 7.23, S 8.85; found C 79.39, H 7.35, S 9.00.

*2,2-Dimesityl-1-(4,5,6,7-tetrahydrobenzo[b]thien-2-yl) ethenol (***E2***)*

A solution of dimesityl ketene (1.28 g, 4.61 mmol) was added to the Grignard reagent prepared freshly from 2-bromo-4,5,6,7-tetrahydrobenzo[*b*]thiophene (1.00 g, 4.61 mmol) in dry Et_2O (15 ml). The reaction mixture was refluxed for 4 – 5 h. The reaction was quenched with NH_4Cl (sat. aq. 30 ml) solution after cooling, extracted with Et_2O (3×25 ml), dried over Na_2SO_4 (anhyd.) and concentrated. A partially pure product was obtained by column chromatography with *n*-hexane/ethyl acetate (10:1) which was recrystallized from EtOH yielding the pure product as a brown solid (560 mg, 1.34 mmol, 29%). **E2**: Mp. 176 – 179 °C. – IR (KBr): $\tilde{\nu} = 3498$ (m, OH), 2927 (s, CH), 2852 (m, CH), 1642 (m, C=C), 1610 (C=C arom), 1440 (s), 1310 (m), 1238 (m), 1160 (m), 1129 (m), 1006 (m), 850 (s) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.76$ (m, 4 H, 5'-H, 6'-H), 2.07, 2.14 and 2.26 (3s, 18 H, coalescence, Mes-CH_3), 2.46 (t, 2 H, $J = 5.6$ Hz, 4'-H), 2.62 (t, 2 H, $J = 5.6$ Hz, 7'-H), 5.01 (s, 1 H, OH), 6.67 (s, 1H, 3'-H), 6.77 (s, 2H, Mes-H), 6.87 (s, 2H, Mes-H). – ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 20.75$, 20.81, 20.94, 21.00, 21.33, 22.85, 23.45, 25.00, 25.36, 110.60, 128.24, 129.33, 129.88, 130.31, 132.15, 134.19, 134.67, 136.34, 136.79, 137.52, 137.64, 138.92, 139.31, 145.25. – $C_{28}H_{32}OS$ (416.62): calcd. C 80.72, H 7.74, S 7.70; found C 80.48, H 7.78, S 7.89.

*2,2-Dimesityl-1-(3-thienyl)ethenol (***E3***)*

Butyllithium (2.5 M, 4.3 ml, 11 mmol) was added dropwise to 3-bromothiophene (3.1 g, 11 mmol) at −70 °C in dry THF (30 ml). After 2 h a crude solution of dimesitylketene (11 mmol) in 15 ml THF was added to the reaction mixture at −70 °C and the reaction was stirred for 12 h at r.t. After quenching with water the reaction mixture was extracted with ether, washed with saturated $NaHCO_3$, dried over Na_2SO_4 (anhyd.) and concentrated. The crude product was purified with column chromatography with a mixture of hexane and ether as eluent (10% ether) yielding a colorless crystalline solid (78%). **E3**: ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.18$ (s, 6 H, *p*-Mes-CH_3), 2.23 and 2.28 (2s, 12 H, o-Mes-CH_3), 5.09 (s, 1H, OH), 6.64 (dd, $J = 1.0$, 5.0 Hz, 1H, 4'-H), 6.73 (bs, 2H, Mes-H), 6.88 (bs, 2H, Mes-H), 7.01 (dd, $J = 3.1$, 5.0 Hz 1H, 5'-H), 7.35 (dd, $J = 1.0$, 3.1 Hz, 1H, 2'-H). – ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 20.68$, 20.72, 20.80, 20.88, 20.91, 20.98, 111.13, 124.94, 127.36, 129.24, 132.38, 135.08, 136.05, 136.97, 137.49, 138.43, 139.11, 146.06. – $C_{24}H_{26}OS$ (362.53): calcd. C 79.51, H 7.23, S 8.85; found C 79.45, H 7.70, S 8.42.

*2,2-Dimesityl-1-(2-furyl)-ethenol (***E4***)*

n-Butyllithium (9.20 ml of a 1.6 M in *n*-hexane) was added to an ice-cooled solution of furan (1.06 ml, 1.00 g, 14.7 mmol) in dry THF (40 ml). The solution was stirred at 0 °C for 30 min. A solution of dimesitylketene (4.09 g, 14.7 mmol) in dry THF (30 ml) was added to the solution and stirred for additional 2 h at 0 °C and at r.t. for 4 h. The reaction was quenched with NH_4Cl (sat aq. 45 ml) solution, extracted with Et_2O (3×25 ml), dried over Na_2SO_4 (anhyd.) and concentrated. The crude product was chromatographed with cyclohexane/ethylacetate (3:1) to furnish the pure product as a brown solid (3.54 g, 10.2 mmol, 70%). **E4**: M.p. 152 – 155 °C. – IR (KBr): $\tilde{\nu} = 3484$ cm^{-1} (s, OH), 2916 (s, CH), 2849 (m), 1654 (w), 1619 (m), 1608 (m), 1543 (s), 1479 (s), 1437 (m), 1197 (s), 1161 (s), 1067 (s), 1015 (s), 854 (s), 745 (s). – ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.97$, 2.17, 2.25 and 2.27 (4 s, coalescence, 18 H, Mes-CH_3), 5.10 (s, 1 H, OH), 5.99 (dd, 1 H, $J = 0.8$, 3.5 Hz, 3'-H), 6.28 (dd, 1 H, $J = 1.8$, 3.5 Hz, 4'-H), 6.76 (s, 2H, Mes-H), 6.87 (s, 2 H, Mes-H), 7.32 (dd, 1H, $J = 0.8$, 1.8 Hz, 5'-H). – ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 20.70$, 20.73, 20.79, 20.82, 20.85, 106.73, 110.96, 111.37, 112.15, 129.25, 129.83, 130.22, 132.09, 134.74, 135.89, 137.17, 138.26, 138.95, 141.55, 142.09, 149.46. – $C_{24}H_{26}O_2$ (346.47): calcd. C 83.20, H 7.56; found C 83.13, H 7.53.

*2,2-Dimesity1-(N-methylpyrrol-2-yl)-ethanone (***K5***)*

n-Butyllithium (1.6 M in *n*-hexane, 7.70 ml, 12.3 mmol) was added dropwise to an ice-cooled solution of *N*-methylpyrrole (1.10 ml, 1.00 g, 12.3 mmol) in dry THF (20 ml). After 90 min a solution of dimesitylketene (3.42 g, 12.3 mmol) in dry THF (25 ml) was added and the reaction mixture was stirred for additional 2 h at 0 °C and 1.5 h at r.t. The reaction mixture was quenched with NH_4Cl solution (sat. aq., 30 ml), extracted with Et_2O (3×25 ml), dried over Na_2SO_4 (anhyd.) and concentrated. The crude product was chromatographed with *n*-hexane/ethyl acetate (3:1) as eluent yielding the ketone **K5** (288 mg, 800 μmol, 7%) as yellow solid, Mp. 148 – 150 °C – IR (KBr) $\tilde{\nu} =$ 2919 cm^{-1} (m, C-H), 1644 (vs, C=O), 1608 (s), 1522 (s); 1455 (s), 1366 (s), 1240 (s), 1209 (s), 1094 (s), 1063 (s), 850 (vs). – ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 2.05$ (s, 12 H, *o*-Mes-CH_3), 2.23 (s, 6 H, *p*-Mes-CH_3), 3.95 (s, 3 H, N-CH_3), 6.01 (dd, 1 H, $J = 2.4$, 4.1 Hz, 3'-H), 6.08 (s, 1 H, C-H), 6.69 (dd, $J = 1.7$, 4.1 Hz, 4'-H), 6.77 (s, 5 H, Mes-H and superimposed 5'-H). – ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 21.11$, 21.69, 38.14, 55.72, 108.36, 118.64, 130.65, 130.74, 131.80, 135.23, 136.21, 137.79, 192.80. – $C_{25}H_{29}NO$ (359.49): calcd. C 83.52, H 8.13, N 3.90; found C 83.16, H 8.14, N 3.71.

*3-Mesityl-2-(2-thienyl)-4,6,7-trimethylbenzo[b]furan (***B1***)*

A solution of $Cu(OTf)_2$ (41.7 mg, 115 μmol) in acetonitrile (3 l) was added to a solution of **E1** (20.8 g, 57.4 μmol) in 3 l of acetonitrile. After 3 h sat. aq. $NaHCO_3$ (2 ml) was added. After extraction with Et_2O (3×10 ml) the organic layer was washed twice with sat. aq. NaCl (2×15 ml), water (10 ml) and dried over Na_2SO_4 (anhyd.) and concentrated. The crude product was chromatographed over silica gel using cyclohexane/dichloromethane (3:1) yielding the benzofuran derivative **B1** as a yellow solid (14.1 mg, 39.1 μmol, 68%). – IR (Film): $\tilde{\nu} = 2919$ cm^{-1} (m, C-H), 2849 (w), 1652 (w), 1608 (w, C=C), 1506 (m), 1456 (m), 1375 (m), 1260 (w), 1114 (m), 1017 (m), 909 (m), 850 (m), 732 (m). – ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 1.92$ (s, 3H, *p*-Mes-CH_3), 2.02 (s, 6H, *o*-Mes-CH_3), 2.37 and 2.39 (2 s, 6 H, 4, 6-Bf-CH_3), 2.49 (s, 3 H, 7-Bf-CH_3), 6.76 (s, 1 H, 5-Bf-H), 6.95 (dd, 1 H, $J = 3.8$, 5.0 Hz, 4'-H), 7.00 (s, 2 H, Mes-H), 7.14 (m_c, 2 H, 3'-H, 5'-H). – ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 11.38$, 17.12, 19.09, 20.24, 21.30, 115.39, 117.02, 123.63, 125.12, 125.33, 126.27, 127.24, 128.40, 128.49, 129.45, 132.85, 133.06, 137.82, 137.92, 145.67, 153.65. – HRMS: (70 eV): calcd. 360.1548 [M^+]; found 360.1553 [M^+].

*3-Mesityl-2-(2-pyridyl)-4,6,7-trimethylbenzo[b]furan (***B6***)*

E6 (11.6 mg, 32.4 μmol) and NOSbF6 (17.2 mg, 64.8 μmol) were separately weighed into different test tubes. 3 ml of acetonitrile were added by means of gas-tight syringes to each test tube. After both compounds had dissolved, the one-electron oxidant solution was given to the enol solution. After 1 min sat. aq. $NaHCO_3$ (1 ml) and CH_2Cl_2 (5 ml) were added. The organic layer was washed twice with sat. aq. NaCl (2×10 ml), dried (Na_2SO_4) and the solvent was removed *in vacuo*. The pure benzofuran **B1** (8.4 mg, 23 μmol, 73%) was obtained by chromatography on silica gel (cyclohexane/dichloromethane, 3:1) as a light yellow solid. – IR (neat): $\tilde{\nu} = 2920$ (s, C-H), 2861 (m), 1579 (s), 1508 (w), 1459 (m), 1436 (m), 1372 (w), 1239 (m), 1129 (m), 1046 (m), 930 (w), 851 (m) cm^{-1}. – ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.86$ (s, 3H, *p*-Mes-CH_3), 2.00 (s, 6H, *p*-Mes-CH_3), 2.38 (s, 6H, 4, 6-Bf-CH_3), 2.58 (s, 3H, 7-Bf-CH_3), 6.78 (s, 1H, 5-Bf-H), 6.98 (s, 2H, Mes-H), 7.04 (dm_c, 1 H, $J = 8.1$ Hz, 3'-H), 7.11 (ddd, 1 H, $J = 7.4$, 5.3, 1.0 Hz, 5'-H), 7.46 (ddd, 1 H, $J = 8.1$, 7.4, 1.6 Hz, 4'-H), 8.69 (ddd, 1 H, $J = 5.3$, 1.6, 1.0 Hz, 6'-H). – ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 11.70$, 17.06, 19.06, 20.22, 21.13, 117.64, 120.28, 121.67, 124.67, 126.49, 128.28, 128.92, 130.13, 130.31, 133.83, 136.23, 137.05, 137.41, 147.20, 149.63, 149.84, 154.27. – HRMS (70 eV): *m/z* calcd. 335.1936 [M^+]; found: 335.1938[M^+].

*5,5'-Bis-[2-(3-mesityl-4,6,7-trimethylbenzo[b]furyl)]-2,2'-bithiophene (***BT1***)*

A solution of $Cu(OTf)_2$ (7.7 mg, 21 μmol) in acetonitrile (3 ml) was added to a solution of benzofuran **B1** (7.7 mg, 21 μmol) in acetonitrile (3 ml). After 30 min 2 ml of sat. aq. $NaHCO_3$ were added, and after extraction with 15 ml of CH_2Cl_2 the organic layer was washed twice with sat. aq. NaCl (2×10 ml), dried over Na_2SO_4 (anhyd.) and concentrated. The pure benzofuran dimer **BT1** (6.8 mg, 9.5 μmol, 90%) was obtained by chromatography on silica gel (cyclohexane/dichloromethane, 3:1) as an intense yellow solid. – ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 1.91$ (s, 6 H, *p*-Mes-CH_3), 2.00 (s, 12 H, *o*-Mes-CH_3), 2.36 and 2.39 (2s, 12 H, 4,6-Bf-CH_3), 2.48 (s, 6 H, 7-Bf-CH_3), 6.75 (s, 2 H, Bf-H-5), 6.87 (d, 2 H, $J = 3.9$ Hz, H-3'), 6.90 (d, 2 H, $J = 3.9$ Hz, H-4'), 6.98 (s, 4 H, Mes-H). – ^{13}C NMR ($CDCl_3$, 50 MHz): $\delta = 11.38$, 17.12, 19.12, 20.24, 21.30, 115.93, 117.02, 117.78, 124.15, 124.33, 126.36, 128.33, 128.46, 129.24, 132.19, 133.06, 136.92, 137.73, 137.86, 144.98, 153.74. – HRMS (70 eV): *m/z* calcd. 718.2939 [M^+]; found 718.2926[M^+].

Crystal structure analyses of ***E2*** *and* ***K5****.*

Details for crystal data, data collection, and refinement are given in Table 6. X-ray data were collected on an Enraf-Nonius-CAD4. The structures were solved using SHELXS-86 and SHELXL-93.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 213535.

These data can be obtained free of charge *via* www.ccdc.cam.uk/const/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB2 1EZ, UK, fax: (+44)1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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