Enol Radical Cations in Solution. 13. First Example of a Radical Dication Rearrangement. One-Electron Oxidation of Dihydrobenzofuranyl Cations Leads to Drastic Rate Enhancement in the Oxidative Benzofuran Formation from Enols

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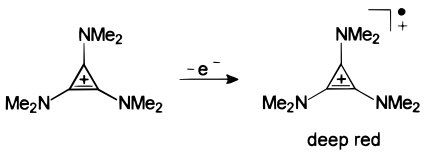
The synthesis and electrochemical investigation of six stable, simple enols **E1**−**E6** are reported that are characterized by electron-releasing substituents in the α-position. Oxidative benzofuran formation from these enols is unusually slow because a key intermediate in the reaction, the dihydrobenzofuranyl cation $\mathbf{X}^+$, is substantially stabilized vs rearrangement by the attached electron-releasing substituents. The persistent cations $\mathbf{X}^+$ were characterized by ^{1}H NMR and cyclic voltammetry, and the kinetics of their rearrangement was followed by UV/vis. Notably, upon one-electron oxidation of $\mathbf{X}^+$ to the radical dication, the formation of the benzofurans **B** was markedly accelerated by a factor of $>10^6$.

Introduction

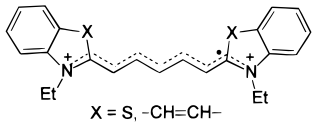
In the context of our ongoing investigations on the chemistry of enol radical cations in solution[1,2] we have discovered the rare event of a selective activation of a cationic intermediate via the corresponding radical dication, which shall be described here in detail.[3] Since radical dications are usually formed through one-electron oxidation of electron-deficient cationic precursors, this class of mostly highly reactive intermediates is difficult to access. Indeed, only a few reports have been concerned with the reactivity[4] and characterization[5] of radical dications.

The first investigation on a radical dication has been reported by *Gerson et al.* in 1971.[5a] After electrochemical oxidation of the stable tris(dimethylamino)cyclopropenyl cation the corresponding deep red radical dication could be identified by its EPR signal.



Some years later *Weiss et al.*[5b] were able to isolate (yields > 90%) the same stable radical dication by the reaction of the tris(dialkylamino)cyclopropenyl cation with antimony pentafluoride and to characterize it. The redox potentials of some tris(dialkylamino)-substituted cyclopropenyl cation/cyclopropenyl radical dication couples were only recently determined by *Taylor et al.*[5d]

A second class of radical dications was investigated by *Lenhard et al.* in 1987.[4a] Electrochemical or chemical one-electron oxidation of cationic dicarbocyanine dyes generated the corresponding radical dications that were found to undergo reversible dimerization at uneven carbon atoms of the methine chain in acetonitrile at room temperature.[4a]



Another class of radical dications is derived from the one-electron oxidation of stable heterocyclic cations such as pyridinium, quinolinium, isoquinolinium, pyrazolium, imidazolium, pyrylium or chalcogenopyrylium cations. According to cyclic voltammetry investigations,[5e,f] in many cases relatively stable radical dications can be detected.

Our earlier investigations[6] on *β*,*β*-dimesityl enols have established that upon oxidation of **E** with 2 equiv of an appropriate one-electron oxidant (e.g., tris(1,10-phenanthroline)iron(III) hexafluorophosphate (**Fephen**), triarylaminium salts), 4,6,7-trimethylbenzofurans **B** were afforded as stable products. The proposed mechanism is shown in Scheme 1).[7]

Kinetic isotope effect studies[1] reveal that OH deprotonation to the corresponding α-carbonyl radicals $\mathbf{R}^\bullet$ constitutes the primary reaction of the enol radical cations $\mathbf{E}^{\bullet+}$. Since the reactions are performed under oxidative conditions, the α-carbonyl radicals $\mathbf{R}^\bullet$, which

(1) Part 12: Schmittel, M.; Langels, A. *J. Chem. Soc., Perkin Trans. 2* **1998**, 565−572.
(2) Schmittel, M.; Gescheidt, G.; Röck, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1961−1963.
(3) Schmittel, M.; Langels, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 392−395.
(4) (a) Lenhard, J. R.; Parton, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 5808−5813. (b) Weiss, R.; Grimmeiss, A. M. H. *Z. Naturforsch.* **1991**, *46b*, 104−110.
(5) (a) Gerson, F.; Plattner, G.; Yoshida, Z. *Mol. Phys.* **1971**, *21*, 1027−1032. (b) Weiss, R.; Schloter, K. *Tetrahedron Lett.* **1975**, 3491−3494. (c) Weiss, R.; Grimmeiss, A. M. H. *Z. Naturforsch.* **1989**, *44b*, 1447−1450. (d) Surman, P. W. J.; Anderson, R. F.; Packer, J. E.; Taylor, M. J. *J. Phys. Chem. A* **1997**, *101*, 2732−2734. (e) Rudenko, A. P.; Pragst, F. *J. Prakt. Chem.* **1983**, *325*, 325−341. (f) Farcasiu, D.; Balaban, A. T.; Bologa, U. L. *Heterocycles* **1994**, *37*, 1165−1192.
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(7) Schmittel, M.; Röck, M. *Chem. Ber.* **1992**, *125*, 1611−1620.

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Scheme 1. Mechanism of the Enol Oxidation

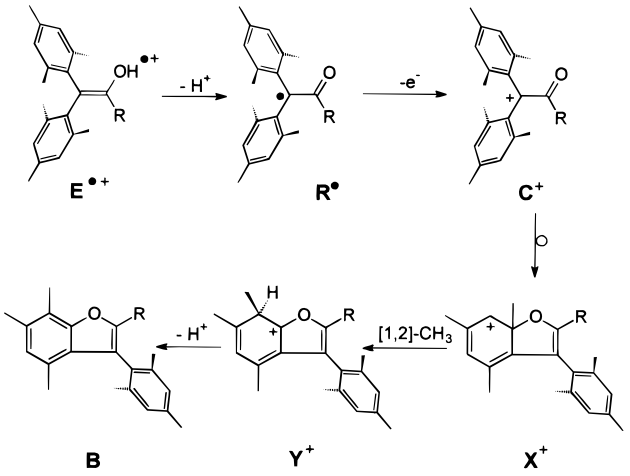


exhibit lower oxidation potentials than the enols,[8] are readily oxidized. The resultant α-carbonyl cations $\mathbf{C}^+$ undergo a rapid Nazarov-type cyclization to the dihydrobenzofuranyl cations $\mathbf{X}^+$, which after a [1,2]-methyl shift and deprotonation furnish the benzofurans **B**.

The [1,2]-methyl shift constitutes the slowest step in the oxidative benzofuran formation and is slower the more electron-releasing the substituent R. The rate constant of the 1,2-methyl shift in the phenyl-substituted dihydrobenzofuranyl cation $\mathbf{X}^+$ (R = Ph) was determined to be $k = 1.8 \times 10^{-4}$ s^{-1} at −20 °C,[9] whereas when stabilization is exerted by a *p*-$C_6H_4NMe_2$ group, the rate constant at room temperature is $k = 2.5 \times 10^{-3}$ s^{-1}.[3]

We now wish to report on the synthesis and the electroanalytical investigations[10] of several novel *β*,*β*-dimesityl enols linked to electron-releasing substituents in the α-position. After oxidation, these enols give rise to the formation of persistent dihydrobenzofuranyl cations $\mathbf{X}^+$, the rearrangement of which to the benzofurans can be markedly accelerated via radical dication intermediates.

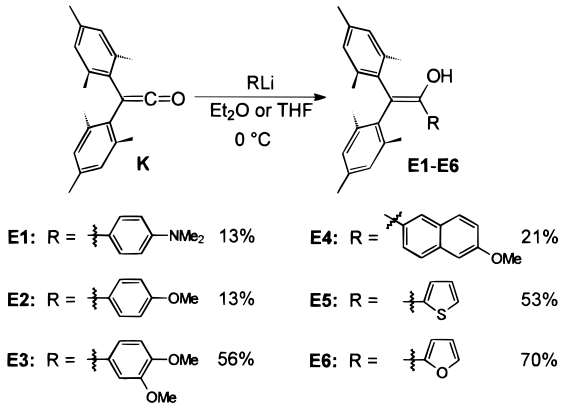
Results

Enols. To stabilize the dihydrobenzofuranyl cation $\mathbf{X}^+$ we have chosen to prepare the *β*,*β*-dimesityl enols **E1**−**E6** with either electron-rich aryl groups or heterocycles[11] in the α-position. The synthesis of enols **E1**−**E6** was straightforward. They were prepared from dimesityl ketene, which was allowed to react with the appropriate lithium reagents, an approach that was originally introduced by *Fuson et al.*[12] and has been used more recently by *Rappoport et al.*[13] The pure enols were obtained in tautomerically pure form after column chromatography and recrystallization from ethanol.

Table 1. Reaction Times, One-Electron Oxidants, and Yields of the Enol Oxidations

	oxidant[a]	reaction time (min)	% of benzofuran **B**	reaction time (h)	% of benzofuran **B**
E1	**TTA**	5	71		
E2	**Fephen**	10	47		
E3	**Cu(OTf)$_2$**	2	12	3	80
E4	**Cu(OTf)$_2$**	1	31	3.5	52
E5	**Cu(OTf)$_2$**	1	22	3.5	68

[a] TTA = tritolylaminium hexafluoroantimonate, Fephen = tris[1,10-phenanthroline]iron(III) hexafluorophosphate, Cu(OTf)$_2$ = copper(II) trifluoromethanesulfonate.



The structures of the enols were assigned on the basis of their characteristic IR, ^{1}H NMR, and ^{13}C NMR spectroscopic data as well as by elemental analysis or high-resolution mass spectrometry since no crystals suitable for X-ray analysis have been obtained so far. The IR spectra of the enols (recorded in KBr) exhibited strong and sharp O−H absorptions around 3500 cm^{-1} and furthermore strong C═C absorptions around 1600 cm^{-1} typical for conjugated systems. The ^{1}H NMR spectra of the enols exhibited only a weak coalescence at room temperature, with sharp singlets being obtained for the OH groups at roughly 5 ppm. The sharp OH absorption in the IR and ^{1}H NMR spectra, the lack of any C═O absorption in the IR and ^{13}C NMR spectra, and a comparison of the spectroscopic data with those of other enols[14] are all in line with their structural assignment as stable simple enols.

Oxidation of the Enols to Benzofurans. Oxidation of enols **E** usually constitutes a fast reaction[15] (reaction time about 1−20 s) that furnishes the anticipated benzofurans **B** in good yields (cf. Scheme 1).[6]

The oxidations of the enols **E1**−**E6** were performed in acetonitrile using 200 mol-% of the appropriate one-electron oxidant, i.e., tri(*p*-tolyl)aminium hexafluoroantimonate (**TTA**, $E_{1/2} = 0.39$ V_{Fc}) or copper(II) triflate (**Cu(OTf)$_2$**, $E_{1/2} = 0.67$ V_{Fc}). The reactions were quenched by adding aqueous $NaHCO_3$ (for reaction times see Table 1), and the pure benzofurans **B** were obtained after column chromatography.

Notably, in the oxidation of enols **E3**−**E5** the amount of formed benzofuran increased with longer reactions

(8) Schmittel, M.; Röck, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1739−1741.

(9) Schmittel, M.; Gescheidt, G.; Eberson, L.; Trenkle, H., *J. Chem. Soc., Perkin Trans. 2* **1997**, 2145−2150.

(10) (a) Heinze, J. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 831−847. (b) Wipf, D. O.; Wightman, R. M. *Anal. Chem.* **1988**, *60*, 2460−2464. (c) Andrieux, C. P.; Hapiot, P.; Saveant, J.-M. *Chem. Rev.* **1990**, *90*, 723−738. (d) Rongfeng, Z.; Evans, D. H. *J. Electroanal. Chem. Interfacial Electrochem.* **1995**, *385*, 201−207. (e) Hu, K.; Evans, D. H. *J. Phys. Chem.* **1996**, *100*, 3030−3036.

(11) Details of the synthesis of **E5** and **E6** are published in the context of the preparation of other stable, simple enols carrying heterocycles. Schmittel, M.; Langels, A. Unpublished results.

(12) Fuson, R. C.; Rowland, S. P. *J. Am. Chem. Soc.* **1943**, *65*, 992−993.

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(15) Schmittel, M.; Baumann, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1961−1963.

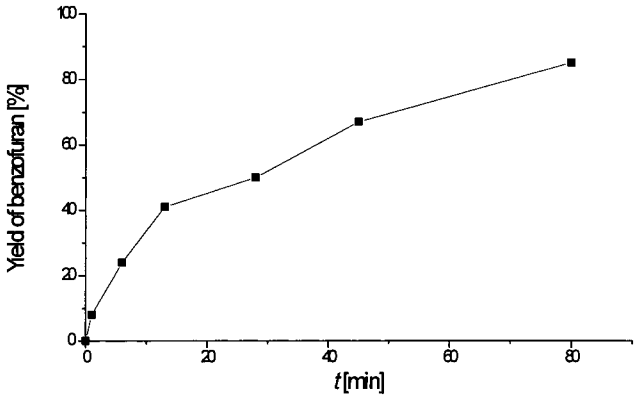


Figure 1. Yield of benzofuran **B3** after different reaction times.

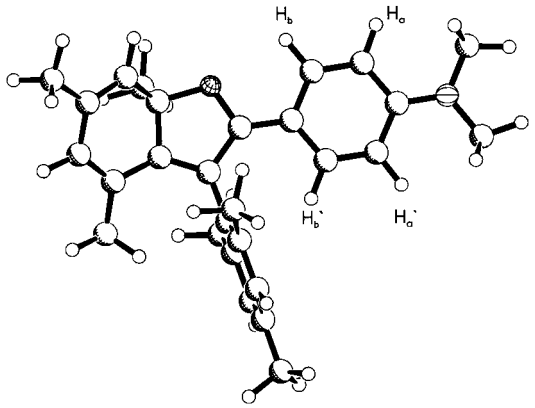


Figure 2. AM1-calculated minimum structure of the dihydrobenzofuranyl cation $\mathbf{X1}^+$.

times, as illustrated in more detail with **E3**. To monitor the time dependence, a larger amount of enol **E3** was oxidized with copper(II) triflate and samples were withdrawn and hydrolyzed at discrete reaction times. The yields were determined by ^{1}H NMR after adding *m*-nitroacetophenone as internal standard. The yield steadily increases until after 80 min finally 80% of the benzofuran **B3** is afforded (Figure 1).

It is noteworthy that the increased yields of **B3** with longer reaction times do not result from the presence of acid. This was shown by a control experiment in which the oxidation was carried out in the presence of trifluoroacetic acid. The yield of **B3** obtained in this experiment was in the same range (**E3**: 17%, 1 min) as in the experiments without acid. The oxidation of the furyl-substituted enol **E6** proved to be much more complex and will be described elsewhere.[11]

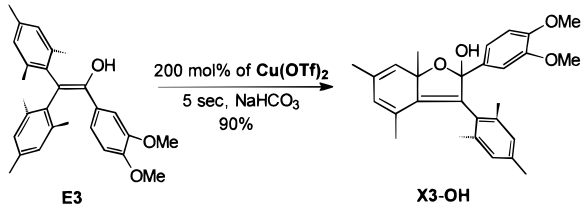
Identification of Dihydrobenzofuranyl Cations as Persistent Intermediates. To characterize the dihydrobenzofuranyl cations by ^{1}H NMR, enols **E1** and **E3** were directly oxidized in the NMR tube. Oxidation of enol **E1** or the enolate **A1** with tris(*p*-bromophenyl)-aminium hexachloroantimonate ($E_{1/2}$ = 0.70 V_{Fc}) or copper(II) triflate in $CDCl_3$ or acetonitrile-d_3 led to the quantitative formation of a species that could be identified as the dihydrobenzofuranyl cation $\mathbf{X1}^+$. The spectra recorded at −15 °C exhibited some interesting features. Characteristically, the signals of the NMe_2 group no longer appear as one singlet but as two singlets (δ = 3.35 and 3.43 ppm). This hints at high barriers for C_{bf}==C_{ar} and C_{ar}==N bond rotation, the double-bond character of which can be rationalized because of the significant stabilization of the cation through the *p*-NMe_2 group.[16]

Furthermore, a doublet (J = 9.8 Hz) for one hydrogen atom showed up downfield (δ = 8.27 ppm), which can be assigned to H_b. In contrast, H_b' resides in the shielding region of the mesityl ring and appears together with H_a and H_a' at δ = 7.04−7.18 ppm (multiplet). The singlets at 6.46 and 6.83 ppm can be assigned to the vinylic protons at the former mesityl ring. Likewise, a new aliphatic methyl group showed up as a singlet at δ = 1.64 ppm, which can be assigned to the methyl group at the 7a-position of the dihydrobenzofuran ring. The other methyl groups (two methyl groups from the dihydrobenzofuranyl cation and three from the mesityl ring) appear as individual singlets, indicative of the fact that the rotation of the remaining mesityl group is hindered. In agreement with these ^{1}H NMR data, the AM1-calculated[17] minimum structure is characterized by the mesityl group placed almost perpendicular to the *N*,*N*-dimethylaminophenyl unit (Figure 2).

Similarly, enol **E3** in acetonitrile-d_3 was oxidized with the appropriate amount of copper(II) triflate in acetonitrile-d_3 directly in the NMR tube at room temperature.

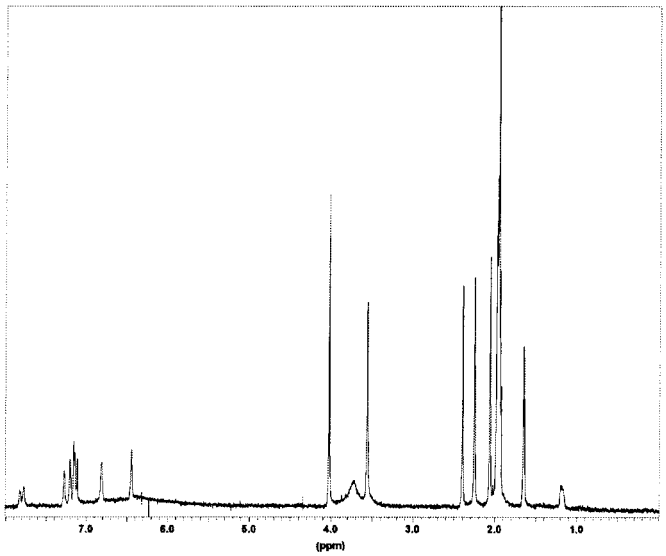
The spectrum exhibits seven signals in the aromatic and vinylic region and several different methyl groups (Figure 3). Unfortunately, two methyl groups coincide with the signal of the solvent. The signals at 6.44 and 6.81 ppm belong to the two vinylic protons of the dihydrobenzofuranyl cation. The remaining mesityl ring is no longer able to rotate since two signals are obtained for the two mesityl protons (7.14 and 7.19 ppm). The most indicative signals in the spectra are the singlet at 1.64 ppm and the doublet at 7.79 ppm. The signal at 1.64 ppm can be assigned analogously as in $\mathbf{X1}^+$ to the methyl group at the 7a-position of the dihydrobenzofuranyl ring, whereas the doublet (J = 9.1 Hz) at 7.79 ppm belongs to 6′-H of the 3,4-dimethoxyphenyl ring. The different shifts of 2′-H (appears as doublet at 7.27 ppm) and 6′-H are apparently due to fact that 2′-H resides in the shielding area of the mesityl ring which is placed perpendicular to the 3,4-dimethoxyphenyl group.

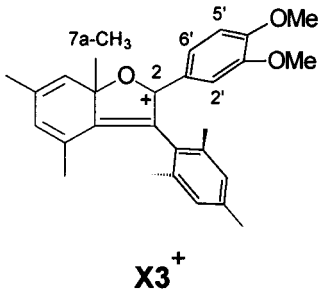
An additional, albeit indirect, structural proof for the occurrence of dihydrobenzofuranyl cations $\mathbf{X}^+$ in the oxidation of the corresponding enols **E1**−**E6** could be obtained by trapping the cation $\mathbf{X3}^+$ with water as its OH adduct. When the oxidation of **E3** with 2 equiv of copper(II) triflate in acetonitrile was immediately quenched by adding aqueous $NaHCO_3$ solution, product **X3**−**OH** could be intercepted. It was isolated in 90% yield after column chromatography and characterized by ^{1}H NMR, ^{13}C NMR, IR, and MS.



A second, but low-yield trapping product could be characterized only by ^{1}H NMR spectroscopy. In the

(16) Analogously in structurally related ammonium ions hindered rotation about the C==N bond was reported. Pindur, U. *Arch. Pharm. (Weinheim, Ger.)* **1980**, *313*, 301−306.





X3$^+$

Figure 3. ^{1}H NMR spectra of the dihydrobenzofuranyl cation **X3**$^+$.

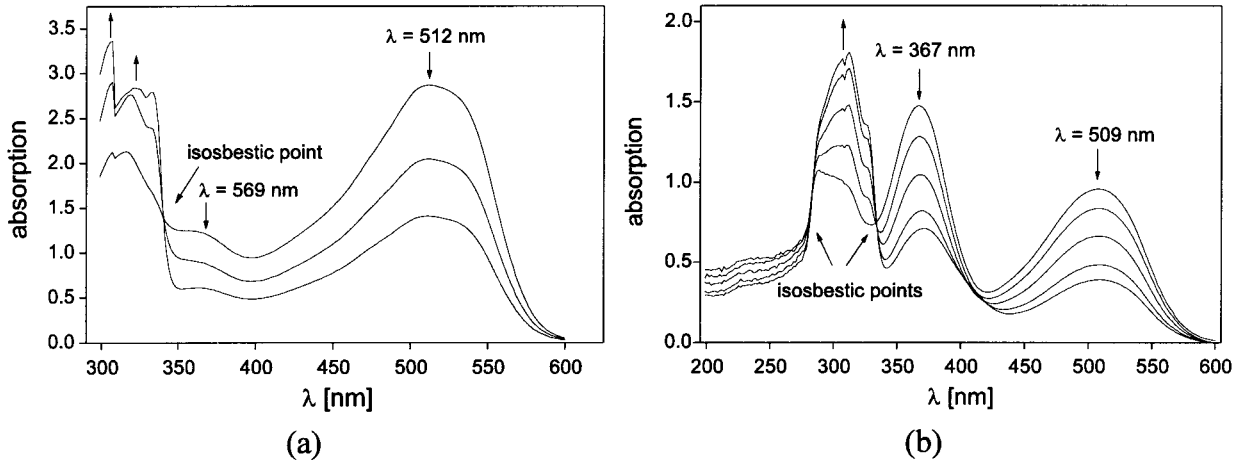


Figure 4. UV/vis spectra of (a) cation **X3**$^+$ and (b) cation **X6**$^+$ in acetonitrile at different times.

second isomer, the hydroxyl group is placed in the 3a-position of the dihydrobenzofuranyl ring. Cyclic voltammetry investigations revealed for **X3**−**OH** an irreversible peak potential $E_{pa} = 0.92$ V_{Fc} in acetonitrile at $v =$ 100 mV s^{-1}. Notably, **X3**−**OH** could be transformed in 84% yield to the corresponding benzofuran **B3** by addition of excess trifluoroacetic acid (2 h at room temperature).

Persistency of the Dihydrobenzofuranyl Cations X$^+$. The disappearance of the dihydrobenzofuranyl cations **X**$^+$ was kinetically followed by UV/vis spectroscopy. Cations **X**$^+$ were prepared directly in the UV cell by adding an appropriate amount of the dissolved oxidant to the enol solution. In general, the dihydrobenzofuranyl cations **X**$^+$ exhibited two absorption bands around 500 and 370 nm in acetonitrile, which decreased continuously with time. Hence, the determination of their half-life $t_{1/2}$ was accomplished by following the decay of their absorption at a fixed wavelength (Table 2). During the kinetic investigations also the formation of the corresponding benzofurans **B**, could be monitored, since the emerging absorption bands at 320−330 nm were unambiguously assigned to **B** as proven by their independent UV/vis characterization (Figure 4).

Table 2. Determination of the Rate Constant *k* and the Half-Life $t_{1/2}$ of Cations X1$^+$, X3$^+$, X5$^+$, and X6$^+$

cation	k (min^{-1})	$t_{1/2}$ (min)	wave length (nm)	isosbestic point (nm)
X1$^+$	1.50×10^{-1}	4.6[a]		
X3$^+$	2.28×10^{-2}	30.4[b]	512	340
X5$^+$	3.78×10^{-2}	18.3[b]	512	350
X6$^+$	4.00×10^{-2}	17.3[b]	509	282, 334

[a] Determined by ^{1}H NMR kinetics. [b] Determined by UV/vis kinetics.

Interestingly, the dihydrobenzofuranyl cation **X6**$^+$ provided similar UV/vis spectra, although the anticipated benzofuran **B6** could not be detected in preparative oxidation experiments with enol **E6**.[11]

To prepare **X1**$^+$, enolate **A1** was oxidized in order to circumvent problems resulting from protonation at the nitrogen that arise when starting from **E1**. However, oxidation of enolate **A1** did not lead to the clean formation of benzofuran **B1**. Since some of the products exhibited absorption bands almost identical to the dihydrobenzofuranyl cation **X1**$^+$, we could not use the UV/vis technique here. Instead the half-life of dihydrobenzofuranyl cation **X1**$^+$ was determined by ^{1}H NMR kinetic investigations to $t_{1/2} = 4.6$ min at room temperature.

(17) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902−3909.

Table 3. Oxidation Potentials of Benzofurans B at ν = 100 mV s^{-1} in Acetonitrile and Dichloromethane/TFAN

	CH_3CN		CH_2Cl_2/TFAN	
benzofuran	$E_{1/2}$(**B**) (V_{Fc})	E_{pa}($\mathbf{B}^{\bullet+}$) (V_{Fc})	$E_{1/2}$(**B**) (V_{Fc})	E_{pa}($\mathbf{B}^{\bullet+}$) (V_{Fc})
B1	0.23	0.72[a]	*b*	*b*
B2	0.69[c]	*b*	*b*	*b*
B3	0.65	1.02	0.56	1.08
B4	0.71	1.07	0.63	1.08
B5	0.68	*d*	*b*	*b*

[a] Partially reversible, no follow-up products detectable. [b] Not determined. [c] Only partially reversible. [d] The radical cation of the benzofuran **B5** dimerizes to the bithiophene derivative. Schmittel, M.; Langels, A. Unpublished Results.

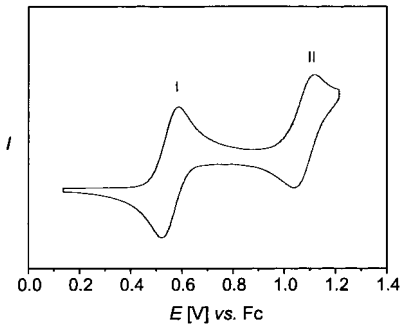


Figure 5. Cyclic voltammogram of **B3** in dichloromethane/trifluoroacetic anhydride (ν = 100 mV s^{-1}, c = 1 mM, working electrode = 1 mm platinum disk, counter electrode = platinum wire, reference electrode = silver wire).

Cyclic Voltammetry of the Benzofurans. The cyclic voltammetry investigations of the electron-rich benzofurans exhibited several new aspects.[6,8] Usually, only a single, reversible oxidation wave is obtained in the CV for the benzofurans at about 0.81−0.99 V_{Fc}.[8] The benzofurans **B1**−**B5** are reversibly oxidized at distinctively lower potentials due to the electron-releasing character of their substituents, but most notably, the first oxidation wave of the benzofurans is followed by a second one. The second wave constitutes the oxidation of the benzofuran radical cations $\mathbf{B}^{\bullet+}$ to the corresponding dications $\mathbf{B}^{2+}$ (Table 3).

In the case of benzofuran **B1**, the second wave is partially reversible in acetonitrile, whereas for the benzofurans **B3** and **B4** the second oxidation wave is irreversible. Small reduction waves could only be monitored at 0 °C in acetonitrile or at higher scan rates (ν = 1 or 2 V s^{-1}). However, when performing the CV experiments in dichloromethane or in dichloromethane with added trifluoroacetic anhydride (TFAN), reversibility was attained for both redox steps (Figure 5), allowing the determination of the thermodynamic half-wave potentials for $\mathbf{B}^{\bullet+}$ to $\mathbf{B}^{2+}$ even at low scan rates ($\nu \geq$ 50 mV s^{-1}).

Cyclic Voltammetry of the Enols. The enols **E1**−**E6** were submitted to cyclic voltammetry experiments at different scan rates. In standard cyclic voltammetry investigations irreversible oxidation waves were monitored for all enols at scan rates between 20 and 500 mV s^{-1}, indicative of fast follow-up reactions (deprotonation, see Scheme 1) of the generated enol radical cations. Noticeably, all enols displayed an additional irreversible oxidation wave at higher anodic potential, which is uniformly placed 0.9−1.2 V above the first oxidation wave. In dichloromethane as solvent again two irreversible oxidation waves emerged. Once more for all systems **E1**−**E6**, the potential difference between the two oxidation waves is 0.9−1.1 V (Figure 6).

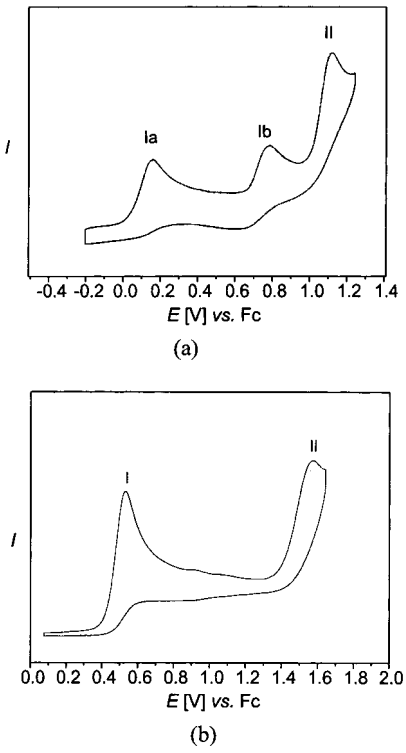
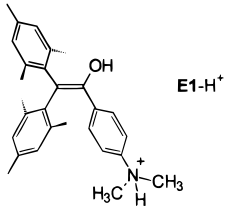


Figure 6. Cyclic voltammograms of (a) **E1** and (b) **E3** (ν = 100 mV s^{-1}, c = 1 mM in acetonitrile, working electrode = 1 mm platinum disk, counter electrode = platinum wire, reference electrode = silver wire).

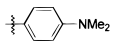
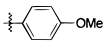
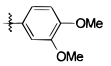
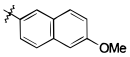
Among the model compounds, enol **E1** occupies a special place since the cyclic voltammogram (CV) of enol **E1** exhibited *two* additional oxidation waves besides the first oxidation wave. The second wave at E_{pa} = 0.76 V_{Fc} (wave Ib in Figure 6a) in the CV of **E1** could be readily assigned to the oxidation of the protonated enol $\mathbf{E1}-\mathbf{H}^+$ by control experiments in the presence of added base (4-*N*,*N*-(dimethylamino)pyridine) and acid (trifluoromethanesulfonic acid). The oxidation chemistry of $\mathbf{E1}-\mathbf{H}^+$ has already been extensively described and shall not be repeated here.[3] Wave II in the CV of enol **E1** seems to correspond to the second waves in the CVs of the other enols as judged by its anodic shift vs **E1** (Table 4).



Since in earlier investigations the dihydrobenzofuranyl cations $\mathbf{X}^+$ of two systems (R = Ph, *p*-$C_6H_4NMe_2$)[2,9] had proved to be rather long-lived, we supposed that the additional wave in the cyclic voltammograms of **E1**−**E6** was due to the oxidation of $\mathbf{X1}^+-\mathbf{X6}^+$. When enols **E1**, **E3**, and **E4** were submitted to multisweep cyclic volta-

(18) When scanning beyond the second wave, fast coating of the electrode hampered the multisweep cyclic investigations of **E5** and **E6**.

Table 4. Oxidation Potentials of Enols E1−E6 and Dihydrobenzofuranyl Cations X1$^+$−X6$^+$ at ν = 100 mV s^{-1}

Compound		CH_3CN		CH_2Cl_2	
	R	E_{pa} (**E**)	E_{pa} ($\mathbf{X}^+$)	E_{pa} (**E**)	E_{pa} ($\mathbf{X}^+$)
1:		0.13 V_{Fc}	1.10 V_{Fc}	—[a]	—[a]
2:		0.51 V_{Fc}	1.66 V_{Fc}	—[a]	—[a]
3:		0.51 V_{Fc}	1.54 V_{Fc}	0.58 V_{Fc}	1.54 V_{Fc}
4:		0.52 V_{Fc}	1.41 V_{Fc}	0.64 V_{Fc}	1.52 V_{Fc}
5:		0.53 V_{Fc}	1.80 V_{Fc}	0.64 V_{Fc}	1.76 V_{Fc}
6:		0.53 V_{Fc}	1.79 V_{Fc}	0.63 V_{Fc}	1.73 V_{Fc}

[a] Not determined.

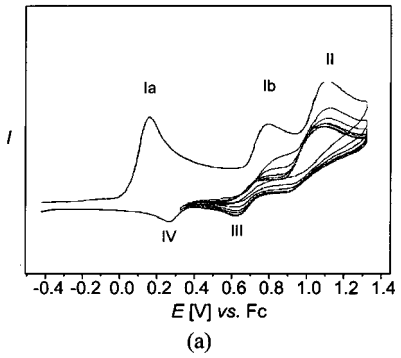


Figure 7. Multisweep cyclic voltammograms of (a) **E1** (ν = 500 mV s^{-1}, c = 1 mM in acetonitrile) and (b) **E3** (ν = 500 mV s^{-1}, c = 1 mM in dichloromethane/trifluoroacetic anhydride); working electrode = 1 mm platinum disk, counter electrode = platinum wire, reference electrode = silver wire.

mmogram investigations at the anodic potential of the second wave,[18] the formation of two new waves could be detected (Figure 7).

The new waves were unambiguously assigned to the corresponding benzofurans (vide supra). For enol **E1** only the reduction waves could be detected (see Figure 7a) due

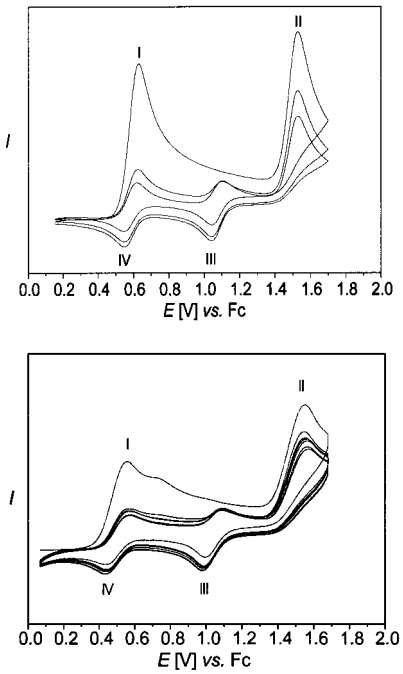


Figure 8. Multisweep cyclic voltammograms of **E3**: (top) digital simulation; (bottom) experiment in dichloromethane/trifluoroacetic anhydride.

to complex protonation/deprotonation equilibria.[3] But in the CV of enol **E3**[19] two reversible redox waves emerged belonging to the oxidation (reduction) of the formed benzofuran **B3** (see Figure 7b). This was also the case when investigating **E4** in dichloromethane.

Digital simulation of the multisweep cyclic voltammogram of enol **E3** using the implicit Crank−Nicholson technique[20] showed good agreement with the experimental curve based on an ECECEC mechanism (see Schemes 1 and 2). A comparison of the experimental curve (disregarding the extra wave caused by enol protonation at E_{pa} = 0.76 V_{Fc}) and the simulated curve indicated that especially the current intensities of the formed benzofuran **B3** and the corresponding radical cation **B3**$^{\bullet+}$ were reproduced very well (Figure 8).

The oxidation potentials of **X1**$^+$ and **X3**$^+$ could also be determined in independent cyclic voltammetry investigations. When the corresponding enols **E1** and **E3** were oxidized with 2 equiv of a one-electron oxidant and when the CVs of the resultant solution were immediately recorded in acetonitrile, an irreversible wave appeared at 1.12 V_{Fc} for **X1**$^+$, whereas for **X3**$^+$ an irreversible wave at 1.55 V_{Fc} could be monitored.

Discussion

Enol Oxidation. At first glance oxidation of electron-rich enols **E1**−**E6** seems to follow the well-established mechanistic pattern outlined in Scheme 1, although reaction times proved to be much longer than observed earlier. In contrast to less electron-rich β,β-dimesityl enols,[15] however, none of the cyclic voltammograms exhibited any benzofuran formation on the time scale of the cyclic voltammetry experiment but instead displayed a new oxidation wave. Notably, the second wave exhibits the same anodic peak current as the enol oxidation wave (see Table 5). Since the enol wave is characterized by an ECE process (two electrons consumed), the second

(19) Unfortunately the enol oxidation wave in dichloromethane splits up into two oxidation waves after some time. Supposedly a protonated species emerges since the wave disappears in the presence of base. Another severe problem in this MS CV experiment was the coating of the electrode after scanning the second wave.

(20) (a) Lasia, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *146*, 397−411. (b) Heinze, J.; Störzbach, M.; Mortensen, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *165*, 61−70. (c) Heinze, J.; Störzbach, M. *J. Electroanal. Chem. Interfacial Electrochem.* **1993**, *346*, 1−27.

Table 5. Comparison of the Anodic Peak Currents of Wave I and Wave II in the CVs of the Enols E1 and E3−E6

scan rate (mV s^{-1})	I_{pa}(wave I)/I_{pa}(wave II) of			
	E3	**E4**	**E5**	**E6**
50	1.0:0.9	1.0:1.0	1.0:0.8	1.0:0.9
100	1.0:0.9	1.0:1.0	1.0:0.8	1.0:0.8
200	1.0:0.9	1.0:1.0	1.0:0.8	1.0:0.8
500	1.0:0.9	1.0:1.0	1.0:0.9	1.0:0.8

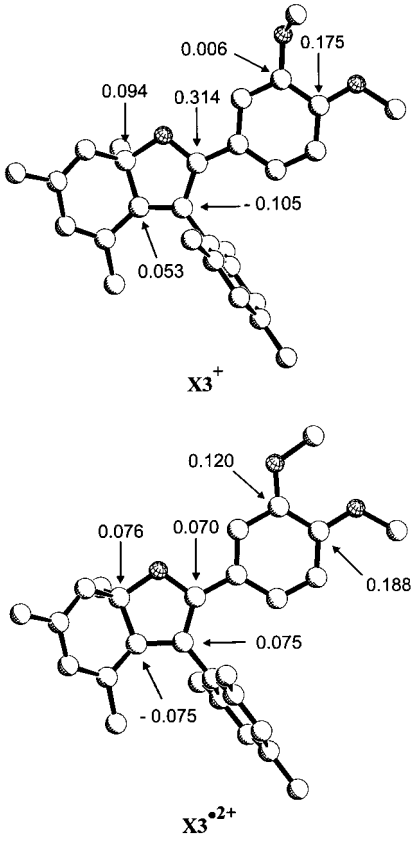


Figure 9. AM1-calculated charge density in the cyclohexadienyl cation $\mathbf{X3}^+$ and the corresponding radical dication $\mathbf{X3}^{\bullet 2+}$.

wave should equally correspond to an overall two-electron-transfer process.

For all model systems the second wave is shifted 0.9−1.2 V anodically vs the enol wave (Table 4). This proposes that an intermediate on the way to the benzofuran **B** is rather long-lived and its oxidation wave is therefore observable in the cyclic voltammetry investigations.

Dihydrobenzofuranyl Cations. The long-lived intermediate in the oxidative transformation could be unambiguously assigned as the dihydrobenzofuranyl cation $\mathbf{X1}^+$−$\mathbf{X6}^+$. The structural assignment is based (1) on direct NMR evidence for dihydrobenzofuranyl cations $\mathbf{X1}^+$and $\mathbf{X3}^+$ and (2) on trapping $\mathbf{X3}^+$ with water providing the OH adducts **X3**−**OH** and its isomer in basically quantitative yield.

AM1 calculations[17] on $\mathbf{X3}^+$ (Figure 9) indeed reveal that the positive charge is placed next to the oxygen atom in the furan ring (2-position), which is the preferred position for attack of water as a nucleophile leading to **X3**−**OH**.

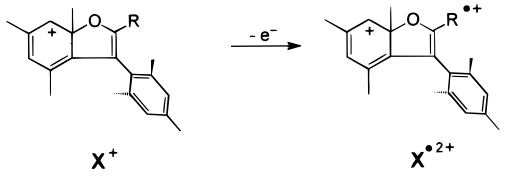
The half-life of $\mathbf{X1}^+$, $\mathbf{X3}^+$, $\mathbf{X5}^+$, and $\mathbf{X6}^+$ has been measured either by UV/vis or by ^{1}H NMR (Table 2). The dihydrobenzofuranyl cation $\mathbf{X3}^+$ constitutes the most stable cation ($t_{1/2}$ = 30.4 min) in this series, whereas the cation $\mathbf{X1}^+$ exhibited the shortest half-life ($t_{1/2}$ = 4.6 min). This difference in half-life compared to $\mathbf{X3}^+$ is not easy to rationalize at first since a *p*-Me_2N group in $\mathbf{X1}^+$ should be a much better electron donor than the methoxy groups. But in this case protonation/deprotonation equilibria in $\mathbf{X1}^+$ complicate the situation.[3] Protons that are released in the oxidation process lead to protonation of the NMe_2 group and thus change the electronic nature of the substituent (from electron releasing to electron withdrawing). In the protonated $\mathbf{X1}$−$\mathbf{H}^+$ the [1,2]-methyl migration is very rapid.

The half-lives of the thienyl-substituted cation $\mathbf{X5}^+$ and the furyl-substituted $\mathbf{X6}^+$ are almost identical. The fact that thiophene stabilizes the cationic charge a bit better than its oxygen analogue is expected in the light of their electronic nature as jugded by the difference of the oxidation potentials of thiophene and furan.[21]

Altogether, the investigations demonstrate that the dihydrobenzofuranyl cations $\mathbf{X1}^+$−$\mathbf{X6}^+$ are well stabilized by the electron-releasing substituents, with the consequence that the [1,2]-methyl shift only occurs very slowly. The persistency of the cations $\mathbf{X3}^+$−$\mathbf{X5}^+$ is also the reason for the longer reaction times (2 h instead of several minutes) needed in the preparative one-electron oxidations of the enols **E3**−**E5**.

A special situation is given with **E6**. The UV/vis spectroscopic investigations indicate that the benzofuran **B6** is indeed initially formed, but in the preparative oxidation the benzofuran could not be detected. This is most likely due to follow-up reactions, presumably caused by protons that are released in the reaction course. One could envisage that the furan ring opens in the presence of acid (enol ether cleavage) leading to polymerization.[11]

Radical Dications as Intermediates in the Benzofuran Formation. We have observed in all cyclic voltammetry investigations on enols **E1**−**E6** a new oxidation wave that can now be assigned to the oxidation of $\mathbf{X}^+$.



This assignment is based on several observations.

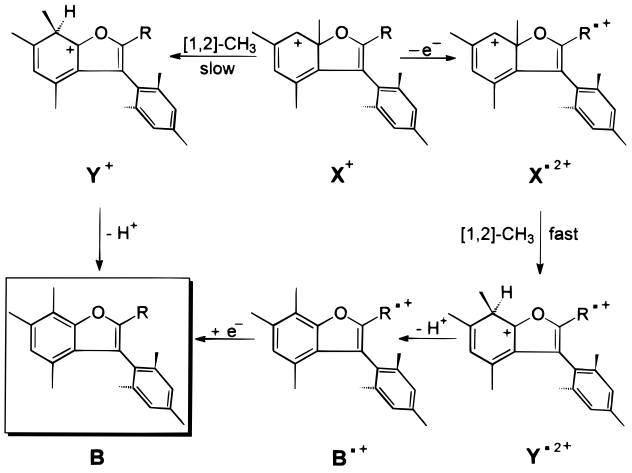
(1) Dihydrobenzofuranyl cations obtained in preparative oxidations and identified by ^{1}H NMR exhibited oxidation waves at potentials identical to waves II in the oxidations of the corresponding enols.

(2) The oxidation potentials of $\mathbf{X3}^+$−$\mathbf{X6}^+$ proved to be identical in acetonitrile and dichloromethane (see Table 4). This observation excludes the possibility of strong acetonitrile complexation to $\mathbf{X}^+$ (in acetonitrile as solvent) and the occurrence of nitrilium adducts.

(3) The oxidation potential of **X3**−**OH** (E_{pa} = 0.91 V_{Fc}) differed markedly from that of wave II (E_{pa} = 1.54 V_{Fc}) in the enol **E3** oxidation. This demonstrates that alcohols **X**−**OH**, possibly formed by spurious traces of water in either acetonitrile or dichloromethane, cannot be responsible for the formation of waves II.

(21) Mizuno, K.; Ishii, M.; Otsuji, Y. *J. Am. Chem. Soc.* **1981**, *103*, 5570−5572.

Scheme 2. Reaction Pathways of X^+ and $X^{\bullet 2+}$



(4) Benzofuran formation could be monitored in cyclic voltammetry experiments starting with $\mathbf{X3}^+$. For that purpose enol **E3** was oxidized directly in the cyclic voltammetry cell with 2 equiv of $\mathbf{NOSbF_6}$. After adding the oxidant the resultant deep red solution exhibited an irreversible oxidation wave at $E_{pa} = 1.55$ V_{Fc}, which decreased slowly ($t_{1/2}$ = several minutes). With this wave decreasing two new waves emerged which belonged to the benzofuran **B3** and also the color of the solutions slowly turned brighter.

The multisweep cyclic voltammetry investigations clearly indicate that upon scanning up to wave II in the enol oxidation, that is after anodic oxidation of $\mathbf{X1}^+$, $\mathbf{X3}^+$, and $\mathbf{X4}^+$, the corresponding benzofurans are formed rapidly. The assignment of the new waves to the benzofurans **B** is straightforward and basically double-checked, because it is based on two emerging reduction waves, one for $\mathbf{B}^{2+}$ and one for $\mathbf{B}^{\bullet +}$ reduction.

The cyclic voltammetry and preparative oxidation investigations now indicate unambiguously that both species ($\mathbf{X}^+$ and $\mathbf{X}^{\bullet 2+}$) yield the same product although with significantly different reaction times. Hence, the formation of benzofurans **B** starting from $\mathbf{X}^+$ can be accelerated by selectively activating the stable cations $\mathbf{X}^+$ by one-electron oxidation to their corresponding radical dications $\mathbf{X}^{\bullet 2+}$. The very reactive radical dication $\mathbf{X}^{\bullet 2+}$ undergoes a fast [1,2]-methyl shift followed by deprotonation to provide the benzofuran radical cation $\mathbf{B}^{\bullet +}$, which is immediately oxidized at the applied potential to the dication $\mathbf{B}^{2+}$. The latter is rather persistent ($k = 3 \times 10^{-2}$ s^{-1} for $\mathbf{B3}^{2+}$ and 1 s^{-1} for $\mathbf{B4}^{2+}$ in dichloromethane/TFAN) and can be reduced twice to the neutral benzofuran **B** via the benzofuran radical cation $\mathbf{B}^{\bullet +}$ (Scheme 2).

From the fact that in fast scan cyclic voltammetry investigations of enol **E3** in acetonitrile no reduction wave is obtained (up to a scan rate of 200 V s^{-1}) for the oxidation of $\mathbf{X3}^+$ to the corresponding radical dication $\mathbf{X3}^{\bullet 2+}$(wave II) it can be concluded that the follow-up reaction of $\mathbf{X3}^{\bullet 2+}$ is very fast ($k > 200$ s^{-1}). A comparison with the rate constant for $\mathbf{X3}^+$ ($k = 3.8 \times 10^{-4}$ s^{-1}) determined by UV/vis shows that the formation of the benzofuran **B3** is at least accelerated by a factor of 10^6. The reason for this acceleration can be seen in the dramatic change of the electronic situation. Since the electron-releasing substituent is transformed to an electron-withdrawing substituent $\mathbf{R}^{\bullet +}$, the system is no longer stabilized vs the [1,2]-methyl shift. On the other hand, it might be possible that the increased reactivity is due to an inherently higher reactivity of the radical dications $\mathbf{X}^{\bullet 2+}$ compared to the cations $\mathbf{X}^+$ as a consequence of their odd-electron nature. Such an inherently higher reactivity is characteristic for radical cations when comparing them with their neutral counterparts.[22] It is noteworthy that no common-sense route to benzofuran **B** is conceivable by deprotonation of $\mathbf{X}^{\bullet 2+}$, although the radical dication should be highly acidic.

Besides the high reactivity the radical dications $\mathbf{X}^{\bullet 2+}$ also exhibit a high selectivity. This could be demonstrated with the help of a digital simulation. For the simulation of the multisweep experiments of enol **E3** a set of parameters was selected that reflect a very fast and quantitative transformation of the radical dication $\mathbf{X3}^{\bullet 2+}$ to a persistent benzofuran dication $\mathbf{B3}^{2+}$. Since the simulated and experimental CVs show very good agreement as to what concerns the peak currents of the benzofuran $\mathbf{B3}^{2+}$ and $\mathbf{B3}^{\bullet +}$ (see Figure 8), it can be concluded that indeed the radical dication $\mathbf{X3}^{\bullet 2+}$ reacts to benzofuran **B3** with a high yield.

Summary

Six persistent dihydrobenzofuranyl cations have been investigated by ^{1}H NMR and UV/vis spectroscopy as well as by cyclic voltammetry. For the first time a selective and high-yield rearrangement via radical dications has been unambiguously established. As this reaction was shown to proceed much more rapidly ($>10^6$) than the corresponding rearrangement of the cations, it is certainly fair to ask whether other stable or persistent cations can likewise be rearranged after one-electron oxidation. Theoretical and further experimental work about these rare intermediates is hopefully stimulated by our results.

Experimental Section

Materials. Commercial reagents were purchased from standard chemical suppliers and were used without further purification. Dimesityl ketene was prepared according to ref.[23] Acetonitrile for the cyclic voltammetry investigations and the one-electron oxidation reactions was of HPLC quality (Riedel-de Haen) and was distilled from CaH_2.

Apparatus. Infrared Spectra: Perkin-Elmer 1605 FT-IR infrared spectrophotometer. UV/vis spectra: Varian Cary 1E UV/vis spectrophotometer. For all other instrumentations see ref 1.

Cyclic Voltammetry. In a glovebox tetra(*n*-butyl)ammonium hexafluorophosphate (232 mg, 600 μmol) and the electroactive species (6 μmol) were placed in a thoroughly dried cyclic voltammetry cell. Outside of the box acetonitrile (6.0 mL) was added through a gastight syringe to the cell hooked up to a high-purity argon line, and then a 1 mm platinum disk electrode as working electrode, a Pt wire counter electrode, and a Ag reference electrode were placed into the solution. The cyclic voltammograms were recorded at various scan rates

(22) (a) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer: Berlin, 1987. (b) Roth, H. D. *Acc. Chem. Res.* **1987**, *20*, 343−350. (c) Bauld, N. L. *Tetrahedron* **1989**, *45*, 5307−5363. (d) Amatore, C.; Kochi, J. K. *Adv. Electron-Transfer Chem.* **1991**, *1*, 55−148. (e) Mizuno, K.; Otsuji, Y. *Top. Curr. Chem.* **1994**, *169*, 301−346. (f) Johnston, L. F.; Schepp, N. P. *Pure Appl. Chem.* **1995**, *67*, 71−78. (g) Moeller, K. D. *Top. Curr. Chem.* **1997**, *185*, 49−86. (h) Schmittel, M.; Burghart, A. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2550−2589.

(23) Fuson, R. C.; Rowland, S. P.; Armstrong, C. J.; Chadwick, D. H.; Kneisley, J. W.; Shenk, W. J.; Soper, Q. F. *J. Am. Chem. Soc.* **1945**, *67*, 386-393.

using a manifold of starting and reversal potentials. For determination of the oxidation potentials ferrocene ($E_{1/2} = 0.39$ V_{SCE}) was added as internal standard. For fast scan cyclic voltammetry investigations, 385 mg (1.00 mmol) of supporting electrolyte, 50 μmol of substrate, and 4.0 mL of solvent were used. Fast scan cyclic voltammograms were carried out at 25 μm Au ultramicro electrodes, a Pt wire serving as counter electrode, and a Ag wire as reference electrode. Cyclic voltammograms were recorded using a Princeton Applied Research model 362 potentiostat with an Philips model PM 8271 XYt-recorder for scan rates < 1 V s^{-1}. For fast scan cyclic voltammetry, a Hewlett-Packard (HP) model 3314A function generator was used, connected to a three-electrode potentiostat developed by C. Amatore.[24] Data were recorded by a HP 54510 A digitizing oscilloscope linked to a 486DX33 computer using the Hewlett-Packard data transfer program Scopelink.

UV/Vis Kinetics. A 1 mL portion of acetonitrile and 0.1 mL of the enol solution in acetonitrile ($c \approx 2.5$ mmol L^{-1}) were placed in a UV/vis cell. After adding the appropriate amount (2 equiv) of copper(II) triflate in acetontrile ($c \approx 5$ mmol L^{-1}) the spectra were recorded at room temperature. The determination of the half-life of the dihydrobenzofuranyl cations $\mathbf{X}^+$ was accomplished by following the decay of their absorption at a fixed wavelength at room temperature.

Digital Simulation of the Multisweep Cyclic Voltammogram of Enol E3. The computer simulation of the redox chemistry of enol **E3** was carried out on P166+ computer using the Crank−Nicholson technique[20] and DigiSim.[25] All chemical reactions were assumed to be irreversible first-order processes except the ET equilibria. With a standard diffusion constant of $D = 10^{-5}$ cm^2 s^{-1}, the heterogeneous electron-transfer rate constant of k^0_{hetero} and the rate constants of the chemical steps were varied to achieve the best possible agreement with the experimental curves. Only for the follow-up reaction of the dihydrobenzofuranyl cation $\mathbf{X3}^+$ was the rate constant ($k_f = 2.28 \times 10^{-2}$ min^{-1}) as determined from UV/vis experiments used.

Calculation. The force-field program SYBYL[26] was employed to minimize the energies. The AM1 parameter file was used from VAMP 5.0.[27]

Synthesis. The synthesis of 2,2-dimesityl-1-(4-methoxyphenyl)ethenol (**E2**)[14] and 2-(4-methoxyphenyl)-3-mesityl-4,6,7-trimethylbenzofuran **(B2)**[6] has already been described. The synthesis of 2,2-dimesityl-1-(2-thienyl)ethenol (**E5**), 2,2-dimesityl-1-(2-furyl)ethenol (**E6**), and 2-(2-thienyl)-3-mesityl-4,6,7-trimethylbenzofuran (**B5**) is described elsewhere.[11]

2,2-Dimesityl-1-(*N*,*N*-dimethylaminophenyl)ethenol (E1). To a solution of 4-bromo-*N*,*N*-dimethylaniline (3.30 g, 16.5 mmol) in dry diethyl ether (20 mL) was added dropwise *n*-butyllithium (15.5 mmol, 6.60 mL of a 2.5 M solution in hexane). The reaction mixture was refluxed for 17 h before cooling it to 0 °C. At this temperature, a solution of dimesityl ketene (3.28 g, 11.8 mmol) in dry diethyl ether (25 mL) was added, and then the solution was slowly brought to reflux. After 20 h the mixture was allowed to cool to room temperature before hydrolyzing it with half-saturated NH_4Cl (30 mL). The aqueous layer was extracted with diethyl ether (3 × 35 mL), and the combined organic layers were dried ($MgSO_4$). The solvent was removed in vacuo, and the remaining brown oil purified by chromatography on silica gel (cyclohexane/ethyl acetate 1:1). The pure product crystallized from ethanol affording 480 mg (2.20 mmol, 10%), mp 205−208 °C. IR (KBr): $\nu = 3494$ cm^{-1} (s, O−H), 2912 (m, C−H), 1607 (s, C=C), 1522 (m), 1362 (m), 1236 (m), 1062 (m), 812 (s). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.90, 2.20 and 2.26 (3s, coalescence, 18 H), 2.91 (s, 6 H), 5.05 (s, 1 H), 6.49 (d, $J = 9.0$ Hz, 2 H), 6.67 (s, 2 H), 6.87 (s, 2 H), 7.20 (d, $J = 9.0$ Hz, 2 H). ^{13}C NMR: ($CDCl_3$, 50 MHz): δ 20.69, 20.81, 21.24, 21.33, 40.25, 108.36, 111.32, 129.18, 129.52, 129.73, 129.85, 130.09, 130.24, 133.49, 135.22, 136.40, 138.22, 150.26, 150.80. HRMS: M^+ ($C_{28}H_{33}NO$) calcd 399.2562, found 399.2560.

2,2-Dimesityl-1-(3,4-dimethoxyphenyl)ethenol (E3). A solution of *n*-butyllithium (20.0 mmol, 12.5 mL of a 1.6 M solution in *n*-hexane) was added dropwise to an ice-cooled solution of 4-bromoveratrole (4.34 g, 20.0 mmol) and 20 mL of dry Et_2O. After stirring for 1 h at 0 °C a solution of dimesityl ketene (5.06 g, 20.0 mmol) in dry Et_2O (30 mL) was added, and the whole reaction mixture was stirred for 3 h at this temperature and for another 3 h at room temperature. Then a half-saturated aqueous NH_4Cl (30 mL) solution was added, the aqueous layer was extracted with Et_2O (3 × 50 mL), and the combined organic layers were dried ($NaSO_4$). After removal of the solvent in vacuo the remaining brown oil was chromatographed (cyclohexane/ethyl acetate, 3:1) and recrystallized from EtOH to yield the desired compound as a yellow solid (4.67 g, 11.2 mmol, 56%). **E3**: mp 166−168 °C. IR (KBr): $\nu = 3517$ cm^{-1} (s, O−H), 2998 (m, C−H), 1609 (s, C=C), 1575 (m), 1509 (s), 1320 (m), 1236 (s), 1072 (s), 817 (m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.93, 2.19 and 2.28 (3s, coalescence, 18 H), 3.48 (s, 3 H), 3.84 (s, 3 H), 5.19 (s, 1 H), 6.71 (m, 4 H), 6.90 (bs, 2 H), 7.06 (dd, $J = 8.5$ Hz, $J = 2.1$ Hz, 1 H). ^{13}C NMR: ($CDCl_3$, 50 MHz): δ 20.69, 20.81, 55.18, 55.68, 106.70, 108.75, 110.09, 110.13, 110.43, 111.98, 128.67, 129.21, 132.78, 135.63, 135.73, 136.74, 138.20, 147.55, 148.90, 149.93. Anal. Calcd C 80.73, H 7.74; found C 80.83 H 7.77.

2,2-Dimesityl-1-(6-methoxynaphth-2-yl)ethenol (E4). A solution of 2-bromo-6-methoxynaphthalene (1.44 g, 6.07 mmol) in 15 mL of dry Et_2O was cooled to 0 °C and treated with *n*-butyllithium (6.07 mmol, 3.80 mL of a 1.6 M solution in *n*-hexane). After stirring for 30 min at this temperature a solution of dimesityl ketene (1.69 g, 6.07 mmol) in 25 mL of dry Et_2O was added. The reaction mixture was stirred for another 1 h at 0 °C and for 4 h at room temperature before it was hydrolyzed with half-saturated aqueous NH_4Cl (30 mL). The aqueous phase was extracted with Et_2O (4 × 30 mL), the combined organic layers were dried (Na_2SO_4), and the solvent was evaporated. Column chromatography (cyclohexane/ethyl acetate, 10:1) of the remaining oil yielded the product as a gray-white solid (572 mg, 130 mmol, 21%). **E4**: mp 100−101 °C. IR (KBr): $\nu = 3504$ cm^{-1} (s, O−H), 3490 (s, O−H), 2916 (m, C−H), 1627 (s), 1607 (s, C=C), 1593 (s), 1481 (s), 1390 (m), 1235 (s), 1059 (m), 850 (s). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.92, 2.19 and 2.30 (3 s, coalescence, 18 H), 3.89 (s, 3 H), 5.26 (s, 1 H), 6.67 (s, 2 H), 6.92 (s, 2 H), 7.03 (d, $J = 2.4$ Hz, 1 H) 7.08 (dd, $J = 8.8$ Hz, $J = 2.4$ Hz, 1 H), 7.24 (dd, $J = 8.6$ Hz, $J = 1.5$ Hz, 1 H), 7.43 (d, $J = 8.6$ Hz, 1 H), 7.62 (d, $J = 8.8$ Hz, 1 H), 7.90 (d, $J = 1.5$ Hz, 1 H). ^{13}C NMR: ($CDCl_3$, 63 MHz):[28] δ 20.70, 20.79, 20.84, 55.21, 105.48, 107.87, 111.46, 118.56, 125.64, 126.82, 127.86, 128.40, 129.99, 130.39, 132.89, 134.33, 135.40, 135.77, 136.13, 136.83, 137.44, 138.12, 150.30, 158.06. Anal. Calcd C 85.28, H 7.39; found C 85.06 H 7.53.

2-(*p*−*N*,*N*-Dimethylaminophenyl)-3-mesityl-4,6,7-trimethylbenzofuran (B1). In a glovebox tri(*p*-tolyl)aminium hexafluoroantimonate (44.0 mg, 70.0 μmol) and the enol **E1** (14.0 mg, 35.0 μmol) were placed into two separate test tubes equipped with stirring rods. At a high-purity argon line 3 mL of acetonitrile was added to each test tube to dissolve the reactants. The solution of the one-electron oxidant was then added through a syringe to the solution of the enol. After 5 min the mixture was quenched with 2 mL of saturated aqueous $NaHCO_3$ and diluted with 10 mL of CH_2Cl_2 and 10 mL of H_2O. The aqueous layer was extracted three times with CH_2Cl_2. The combined organic layers were washed with saturated aqueous NaCl and water and dried over Na_2SO_4. Removal of the solvent afforded the crude product, which was purified by chromatography on silica gel (cyclohexane/dichloromethane,

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(28) Due to the nature of the β,β-dimesityl unit the ^{13}C signals often coincide. In enol **E4** the two signals for the *p*-Mes-CH_3 groups coincide.

1:1 and 2:1) furnishing 9.8 mg (25 μmol, 71%) of benzofuran **B1**. IR (KBr): $\nu = 2917$ cm^{-1} (s, C−H), 2848 (m, C−H), 1612 (s, C=C), 1522 (s), 1443 (m), 1355 (m), 1195 (m), 1115 (m), 1064 (w), 854 (w), 820 (m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.85 (s, 3 H), 2.02 (s, 6 H), 2.35 and 2.37 (2 s, 6 H), 2.50 (s, 3 H), 2.93 (s, 6 H), 6.60 (d, $J = 9.2$ Hz, 2 H), 6.71 (s, 1 H), 6.96 (s, 2 H), 7.39 (d, $J = 9.2$ Hz, 2 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 11.41, 17.15, 19.00, 20.39, 21.24, 40.25, 112.14, 113.02, 120.09, 125.21, 125.85, 125.97, 126.21, 127.82, 128.15, 131.09, 131.58, 136.98, 137.79, 148.98, 149.68, 153.23. HRMS: M^+ ($C_{28}H_{31}NO$) calcd 397.2406, found 397.2406.

2-(3,4-Dimethoxyphenyl)-3-mesityl-4,6,7-trimethylbenzofuran (B3). E3 (33.0 mg, 79.2 μmol) and copper(II) triflate (57.3 mg, 158 μmol) were separately weighed into different test tubes. A 3 mL portion of acetonitrile was added by means of gastight syringes to each test tube. When both compounds had dissolved, the one-electron oxidant solution was given to the solution of the enol, and after 1 min 1 mL of saturated $NaHCO_3$ was added. After removal of the solvents in vacuo the remaining crude product was dissolved in diethyl ether and chromatographed (cyclohexane/dichloromethane, 3:1) to yield the pure benzofuran **B3** as a white solid (26.3 mg, 63.5 μmol, 80%). **B3**: IR (KBr): $\nu = 2915$ cm^{-1} (m, C−H), 2861 (w, C−H), 1608 (m, C=C), 1513 (s), 1459 (m), 1266 (s), 1144 (m), 1121 (m), 1027 (s), 858 (s), 806 (s). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.91 (s, 3 H), 2.03 (s, 6 H), 2.35 (s, 3 H), 2.37 (s, 3 H), 2.51 (s, 3 H), 3.55 (s, 3 H), 3.86 (s, 3 H), 6.75 (s, 1 H), 6.81 (d, $J = 8.5$ Hz, 1 H), 6.89 (d, $J = 2.1$ Hz, 1 H), 6.99 (s, 2 H), 7.25 (dd, $J = 8.5$ Hz, $J = 2.1$ Hz, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 11.48, 17.21, 19.06, 20.36, 21.15, 55.20, 55.84, 108.02, 111.20, 114.96, 116.93, 117.66, 124.70, 125.42, 126.12, 128.27, 129.76, 130.97, 132.37, 137.34, 137.76, 148.01, 148.53, 148.71, 153.47. HRMS: M^+ ($C_{28}H_{30}O_3$) calcd 414.2195, found 414.2196.

3-Mesityl-2-(6-methoxynaphth-2-yl)-4,6,7-trimethylbenzofuran (B4). E4 (10.9 mg, 25.0 μmol) and Cutriflat (18.1 mg, 50.0 μmol) were separately weighed into different test tubes. A 3 mL portion of acetonitrile was added by means of gastight syringes. When both compounds had dissolved, the one-electron oxidant solution was given to the solution of the enol, and after 3.5 h 1 mL of saturated $NaHCO_3$ was added. After removal of the solvents in vacuo the remaining crude product was dissolved in diethyl ether and chromatographed (cyclohexane/dichloromethane, 3:1) furnishing the pure benzofuran **B4** as a light yellow solid (5.7 mg, 13 μmol, 52%). IR (KBr): $\nu = 2922$ cm^{-1} (s, C−H), 2849 (m, C−H), 1607 (m, C=C), 1513 (s), 1463 (m), 1250 (m), 1199 (m), 1116 (m), 1033 (s), 855 (m). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.90 (s, 3 H), 2.03 (s, 6 H), 2.39 and 2.41 (2 s, 6 H), 2.57 (s, 3 H), 3.90 (s, 3 H), 6.77 (s, 1 H), 7.00 (s, 2 H), 7.04 (d, $J = 2.4$ Hz, 1 H), 7.10 (dd, J = 8.7 Hz, $J = 2.4$ Hz, 1 H) 7.49 (dd, $J = 8.9$ Hz, $J = 1.7$ Hz, 1 H), 7.58 (d, $J = 8.9$ Hz, 1 H), 7.63 (d, $J = 8.7$ Hz, 1 H), 7.90 (m, 1 H). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 11.55, 17.21, 19.06, 20.42, 21.30, 55.32, 105.68, 116.18, 117.02, 118.93, 123.33, 123.88, 125.45, 126.21, 126.91, 127.12, 128.33, 128.50, 128.85, 130.00, 130.73, 133.83, 136.20, 137.40, 137.61, 148.33, 153.50, 158.30. HRMS: M^+ ($C_{31}H_{30}O_2$) calcd 434.2245, found 434.2246.

2-(3,4-Dimethoxyphenyl)-3-mesityl-4,6,7*a*-trimethyl-2,7*a*-dihydrobenzo[*b*]furan-2-ol. Enol **E3** (137 mg, 329 μmol) and copper(II) triflate (238 mg, 658 μmol) were separately weighed into different flasks. Acetonitrile was added by means of gastight syringes to the enol (10 mL) and to the oxidant (5 mL). When both compounds had dissolved, the one-electron oxidant solution was given to the enol solution and 5 mL of saturated NaHCO3 was immediately added to the deep red solution. The aqueous layer was extracted three times with CH_2Cl_2 (10 mL). After washing with saturated NaCl (3 × 10 mL) the organic layers were dried (Na_2SO_4). Thereafter the solvents were removed in vacuo and the remaining solid was chromatographed (cyclohexane/dichloromethane, 3:1) yielding **X3−OH** as yellow-red solid (128 mg, 29.6 μmol, 90%), mp 73−74 °C. IR (KBr): $\tilde{\nu} = 3474$ (m, O−H), 2918 (m, C−H), 2862 (m, C−H), 1608 (w, C=C), 1514 (s), 1465 (m), 1263 (s), 1165 (m), 1137 (m), 1029 (s), 923 (m), 861 (m), 807 (m), 764 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 200 MHz,): $\delta = 1.09$ (s, 3 H), 1.42 (s, 3 H), 1.69 (s, 3 H), 1.79 (d, $J = 1.5$ Hz, 3 H), 2.22 (s, 3 H), 2.51 (s, 3 H), 2.72 (s, 1 H), 3.50 (s, 3 H), 3.83 (s, 3 H), 5.53 (m_c, 1 H), 5.95 (m_c, 1 H), 6.52 (d, $J = 2.1$ Hz, 1 H), 6.54 (s, 1 H), 6.70 (d, $J = 8.4$ Hz, 1H), 6.87 (s, 1 H), 6.98 (dd, $J = 8.4$ Hz, J = 2.1 Hz, 1H). ^{13}C NMR ($CDCl_3$, 63 MHz): $\delta = 17.69$, 18.21, 18.84, 20.94, 21.15, 29.15, 55.38 (OCH_3), 55.80 (OCH_3), 89.50 (C-2), 109.93, 110.44, 110.93, 118.30, 119.09, 127.27, 127.73, 127.79, 128.15, 128.64, 130.00, 130.31, 130.97, 135.31, 136.58, 137.49, 143.80, 147.80, 148.74. HRMS: M^+ ($C_{28}H_{32}O_4$) calcd 432.2301, found 434.2292.

Investigations in the Presence of Acid. To **X3−OH** (7.7 mg, 18 μmol) dissolved in 3 mL of acetonitrile was added 1 mL of trifluroacetic acid. After 2 h stirring at room temperature the reaction mixture was hydrolyzed by adding saturated $NaHCO_3$ (1 mL). After removing the solvent in vacuo the pure benzofuran **B3** (6.2 mg, 15 μmol, 84%) was afforded.

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Supporting Information Available: ^{1}H NMR data and peak assignments for **E1**, **E3**, **E4**, **B1**, **B3**, **B4**, and **X3−OH** and parameters used for the digital simulation (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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