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First Characterization of Phosphoenol Radical Cations in Solution and the Kinetics of the Mesolytic P–O Bond Cleavage in Sterically Shielded Enoxy-Phosphorus Compounds after One-Electron Oxidation

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Dedicated to Professor Henning Lund on the occasion of his 70th birthday.

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The new phosphoenols **1**–**6** and **9** have been synthesized starting from stable simple enols. Upon chemical or electrochemical oxidation, for the first time phosphoenol radical cations could be characterized in solution by cyclic voltammetry and EPR spectroscopy. The preparative one-electron oxidation of the model systems afforded the benzofurans indicating an unprecedented mesolytic P–O bond cleavage. Using cyclic voltammetry the kinetics of this step was determined in dichloromethane and acetonitrile. A rationale to account for the selectivity of the mesolytic P–O bond cleavage is given. Accordingly, reactive species $^{+}P(OEt)_2$ (**16**) and $^{\cdot}P(=O)(OEt)_2$ (**18**) can be generated selectively by mesolytic cleavage. At high scan rates, the partially reversible oxidation wave $\mathbf{1}^{\cdot+} \rightleftharpoons \mathbf{1}^{++}$ could be monitored indicating that the dication of enol phosphate **1** is relatively stable.

Enol phosphates have recently attracted increasing interest among synthetic chemists as useful precursors to ketenes[1] and since they undergo synthetically helpful cross-coupling reactions with C–C bond formation.[2] However, in comparison with other enol derivatives, such as silyl enol ethers which have proved to constitute versatile carbon nucleophiles, e.g. in the Mukaiyama aldol reaction,[3] enol phosphates have received far less attention.

With regard to electron transfer activation only the one-electron reduction of enol phosphates has been investigated,[4,5] while the one-electron oxidation chemistry of these substrates is still unknown. This is surprising in the light of the interesting chemistry of enol-type radical cations[6] which have been shown to be important intermediates in the α-umpolung of ketones and aldehydes,[7] in diastereoselective carbon–carbon bond formation[8] and in the synthesis of benzofurans.[9] Since many enol functionalities,[10] among which we should quote silyl enol ethers,[10b,c,11] tin enolates,[11j] and titanium enolates,[12] have found interesting uses in various reactions after one-electron oxidation, we have extended our current studies to enoxy phosphorus compounds.

Here we present our results on the P–O bond cleavage in phosphoenol radical cations, being the first examples of such a process.[13] To facilitate the characterization of the radical cations we have used bulky β,β-dimesityl enols as precursors, since the crowded aryl groups exert steric hindrance about the β-carbon in the enol derivative which is doubly helpful: (a) nucleophiles cannot attack at the β-carbon and (b) dimerization at the β-carbon is equally severely impeded. This allowed cyclic voltammetry (CV) and EPR characterization and the kinetic investigation of a new P–O bond cleavage mode.

Results

Synthesis. A convenient method for synthesizing enol phosphates is the Perkow reaction of α-bromo ketones with trialkyl phosphites;[14] however, the above model compounds were prepared from the enolates and the appropriate phosphoryl chlorides (Scheme 2 and

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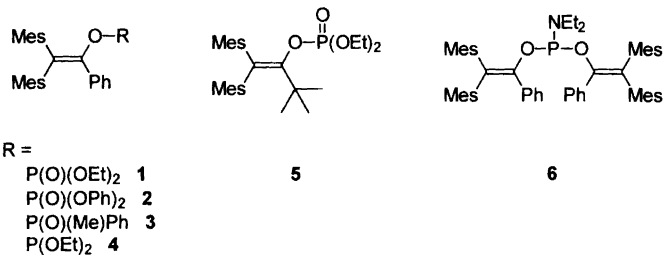
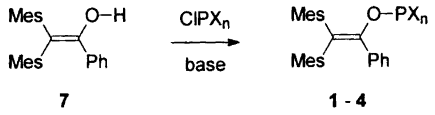


Scheme 1. Phosphoenols **1–6**.



Scheme 2. Synthesis of phosphoenols **1–4** through derivatization of enol **7**.

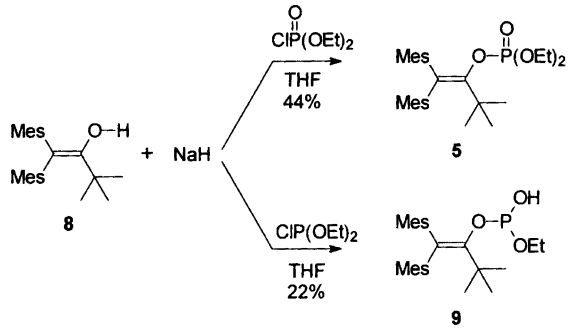
Table 1). The stable simple enols, 2,2-dimesityl-1-phenylethenol (**7**) and 1,1-dimesityl-3,3-dimethylbut-1-en-2-ol (**8**), were used as the starting materials.[15] Remarkably, after reacting enol **8** with NaH and chlorodiethyl phosphite in THF enol phosphite **9** was isolated with a deficiency of one ethoxy group and carrying a hydroxy group instead (Scheme 3).

Bisenol phosphoramidite **6** was synthesized in 34% yield by reacting two equivalents of the enolate of **7** with one equivalent of $ClP(NEt_2)_2$ (**10**). Not only was the chloro substituent in **10** exchanged but also one of the diethylamino groups.

Oxidation potentials. To determine the oxidation potentials[16] (see Table 2)[17] the various phosphoenols were investigated by cyclic voltammetry in acetonitrile. At a scan rate $v = 100\ mV\ s^{-1}$ only irreversible oxidation

Table 1. Reagents and yields for the synthesis of phosphoenols **1–4**.

PX_n	No.	Reagents	Yield (%)
$P(O)(OEt)_2$	**1**	NaH, Cl-P(O)$(OEt)_2$, THF	33
$P(O)(OPh)_2$	**2**	KH, Cl-P(O)$(OPh)_2$, THF	44
P(O)(Me)Ph	**3**	NaH, Cl-P(O)(Me)Ph, THF	29
$P(OEt)_2$	**4**	NEt_3, Cl-P$(OEt)_2$, CH_3CN	35



Scheme 3. Synthesis of phosphoenols **5** and **9**.

Table 2. Anodic peak potentials of phosphoenols **1–6** and **9** in acetonitrile as determined by cyclic voltammetry. The values are referenced to the redox couple ferrocene/ferrocenium.[16,17]

Compound	E_{pa}/V	Compound	E_{pa}/V
1	1.01	**5**	1.22
2	1.10	**6**	0.60
3	0.97	**9**	1.12[b]
4	0.74[a]		

[a] $E^{ox}_{1/2} = 0.86$ V in dichloromethane. [b] In the presence of 100 mol% $(Me_4N)OH$ as base: $E^{ox}_{1/2} = -0.26$ V.

waves were recorded, indicative of a rapid follow-up reaction of the radical cations.

Because of the acidic proton in phosphoenol **9**, it is possible to generate the phosphite anion which can also be oxidized electrochemically by means of cyclic voltammetry. After treatment of **9** with 100 mol% of $(Me_4N)OH$ the color of the solution turned to yellow and a new reversible oxidation wave at low potential was recorded ($E_{1/2} = -0.26$ V).

Cyclic voltammetry (CV). The CV diagnostics[18] of all phosphoenols show mainly two features: (i) a decrease of $i_{pa}v^{-1/2}$ with increasing v is observed (i_{pa}, anodic current; v, sweep rate) and (ii) i_{pc}/i_{pa} increases from 0 to 1 with increasing v. These two features are indicative of an electron transfer step followed by a chemical reaction. Additional evidence was gained through determination of the anodic peak current i_{pa}. The anodic current was referenced to the current of the oxidation wave of enol **7**, which is known to involve two electrons (Table 3).[19]

Through cyclic voltammetry, characteristic oxidation waves of follow-up products were obtained with compounds **1–3**, **5** and **9**. The phenylenol-derived phosphoenols **1–3** display, besides the substrate oxidation wave, a partially reversible oxidation wave at $E_{1/2} = 0.85$ V

Table 3. Anodic peak currents i_{pa} as determined by cyclic voltammetry at $v = 20\ mV\ s^{-1}$ in dichloromethane.

	Enol					
	7	**1**	**2**	**3**	**4**	**5**
Rel. i_{pa}	≡2.0	1.8	1.7	2.0	2.1	1.6

Table 4. $\Delta E_c = E_{pa}$ (second wave) $- E_{1/2}$ (first wave): difference of potential between the first and the second oxidation step in phosphoenols **1–5**, as determined at 100 mV s^{-1}.[17]

	ΔE_c (**1**)/mV	ΔE_c (**2**)/mV	ΔE_c (**3**)/mV	ΔE_c (**4**)/mV	ΔE_c (**5**)/mV
In CH_3CN	180[a]	190[a]	—[b]	—[b]	—[b]
In CH_2Cl_2	230	180	200	200[c]	180

[a]Determined at 1.0 V s^{-1}. [b]Not determined. [c]Determined at 8000 V s^{-1}.

whereas the *tert*-butyl enol-derived phosphoenols **5** and **9** (Fig. 1) exhibit a wave at $E_{1/2} = 0.91$ V.

The oxidation wave of the enol phosphates **1–3** is partially reversible at $v = 100$ mV s^{-1} in dichloromethane and at $v = 500$ mV s^{-1} in acetonitrile. The other phosphoenols exhibit reduction waves only at higher scan rates, e.g. enol phosphite **4** at $v = 4000$ V s^{-1} in dichloromethane. A second, anodically shifted oxidation step was monitored with compounds **1–5** in cases of reversible substrate oxidation waves in dichloromethane and in acetonitrile (Table 4). At high scan rates (3000–5000 V s^{-1}) in dichloromethane the second oxidation wave becomes reversible, as shown for enol phosphate **1** in Fig. 2.

An important mechanistic test is to probe the influence of nucleophiles (e.g. methanol) on the peak current ratio i_{pc}/i_{pa}. Of the phosphoenols **1–5**, only the oxidation waves of enol phosphite **4** are significantly influenced by methanol. Even addition of as little as one equivalent of methanol causes a significant decrease of the reduction wave. In contrast, the reversible oxidation waves of enol phosphates **1**, **2**, **5** and enol phosphinate **3** show deviation from reversibility only upon addition of more than 20 equivalents of methanol.

Kinetics of the mesolytic P–O bond cleavage. As judged by cyclic voltammetry and preparative-scale oxidation results a similar mechanism seems to operate for phosphoenol radical cations (see the Discussion) and for silyl enol ether radical cations investigated previously.[10b] Because two electrons are consumed in the course of the oxidation (Table 3) one further oxidation step must be involved.[10b] Thus, an ECE/DISP mechanism (a rigorous distinction between ECE and DISP mechanism was not made) apparently takes place with a P–O bond cleavage following the one-electron oxidation. By means of digital simulation of the cyclic voltammograms and comparison with the experimental results the rate constants k_f of the follow-up reaction could be derived (Table 5). This rate constant k_f is connected to the P–O bond cleavage of the radical cations and determines its lifetime. The rate of the P–O bond cleavage of the enol phosphate radical cations $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ is about 0.04 to 0.2 s^{-1} in dichloromethane, which is lower than that of enol phosphinate $\mathbf{3}^{\bullet+}$ and again much lower than the rate of enol phosphite $\mathbf{4}^{\bullet+}$. In acetonitrile, the cyclic voltammograms of **4** remain irreversible even at high scan rates of up to 15 000 V s^{-1}, so that only an estimate of $k_f > 10^5$ s^{-1} can be provided.

In order to check for a bimolecular reaction, the reversibility of the oxidation waves in the electrochemical measurements was investigated as function of the

Table 5. Pseudo-first-order rate constants k_f of the reaction following the one-electron oxidation of the phosphoenols **1–5** (P–O bond cleavage).

	k_f/s^{-1}	
Compound	Dichloromethane	Acetonitrile
$\mathbf{1}^{\bullet+}$	3.9×10^{-2}	9.0×10^{-1}
$\mathbf{2}^{\bullet+}$	5.0×10^{-2}	7.0×10^{-1}
$\mathbf{3}^{\bullet+}$	5.0×10^{-1}[a]	5.8×10^{2}
$\mathbf{4}^{\bullet+}$	1.0×10^{4}	$> 10^5$
$\mathbf{5}^{\bullet+}$	0.2[a]	1.1[a]

[a]i_{pc}/i_{pa} is slightly susceptible to substrate concentration, see the text.

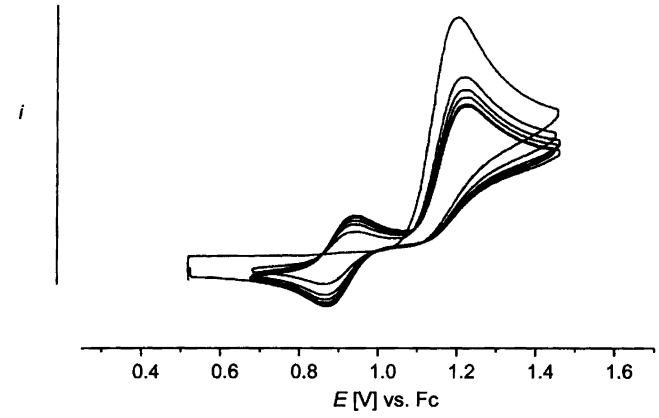


Fig. 1. Multiple sweep CV experiment with compound **9** (acetonitrile, 100 mV s^{-1}).

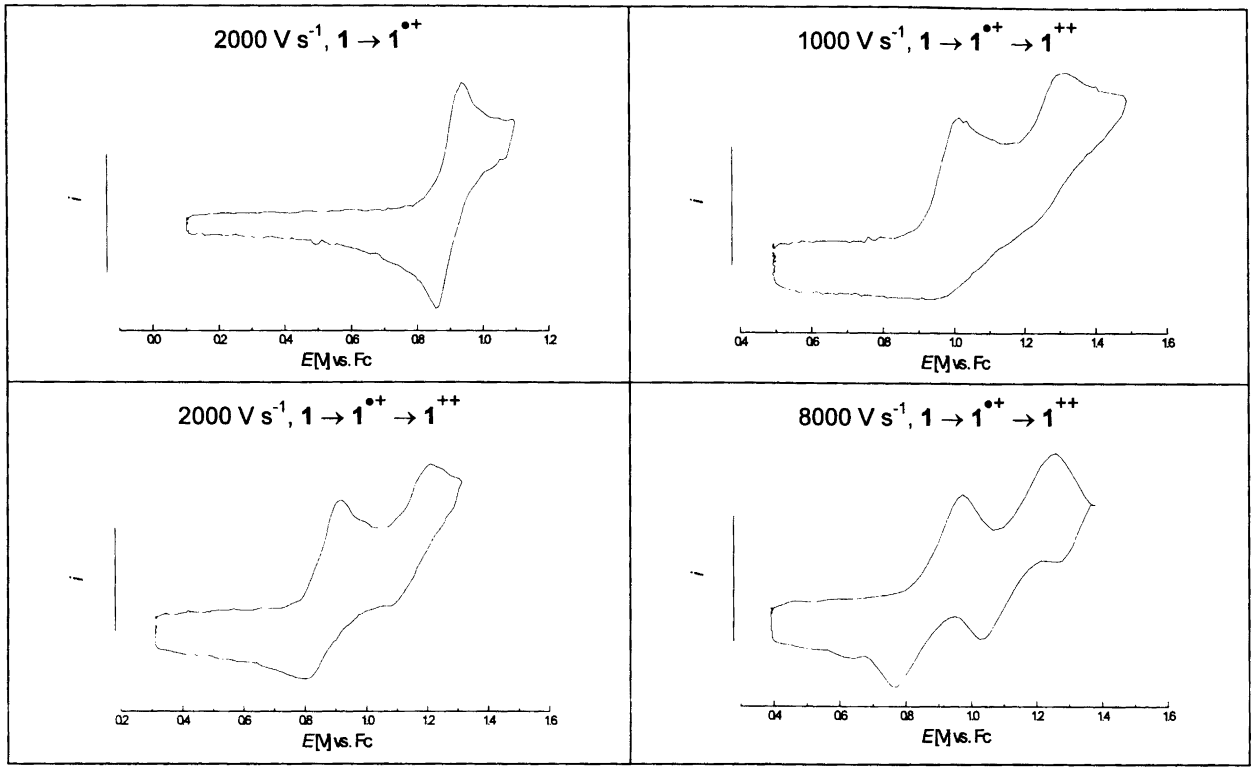
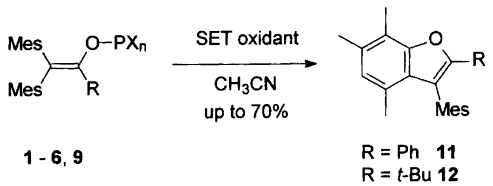


Fig. 2. Oxidation waves of enol phosphate **1** in dichloromethane. Oxidation occurs at $E_{1/2}$ = 0.90 and 1.17 V.

substrate concentration. For compounds **3** (k_f = 5.0×10^{-1} s^{-1} for $c = 6.6 \times 10^{-4}$ M; $k_f = 8.5 \times 10^{-1}$ s^{-1} for $c = 2.2 \times 10^{-3}$ M) and **5** ($k_f = 2.0 \times 10^{-1}$ s^{-1} for c = 6.3×10^{-4} M; $k_f = 2.4 \times 10^{-1}$ s^{-1} for $c = 2.2 \times 10^{-3}$ M) a slight concentration dependence was found but none was found for compounds **1**, **2** and **4**.

Oxidation by chemical oxidants and EPR. The main products of the one-electron oxidation are benzofuran derivatives **11** and **12** as can be seen by cyclic voltammetry and preparative scale one-electron oxidation (Scheme 4 and Table 6). With some substrates, the conversion is low, especially with the enol phosphates **1** and **2**. The yields of benzofurans range from 19 to 70%. Oxidation of bisenolate **6** with 400 mol% of FePhen furnished 72% benzofuran **11** on a molar scale.

To further characterize the radical cations of the phosphoenols, the EPR spectra of compounds **1**$^{\bullet+}$–**3**$^{\bullet+}$ were recorded. To this end, the radical cations were generated through oxidation with O_2AsF_6 in $CHClF_2$ (−100 °C) but only unresolved spectra could be obtained (for g values see Table 7).



1 - 6, 9

R = Ph **11**
R = *t*-Bu **12**

Scheme 4. Oxidation of the phosphoenols **1–6** and **9**.

Table 6. Yields of benzofurans in the oxidation of phosphoenols (reaction in acetonitrile at room temp.; TNPA: tris(*p*-nitrophenyl)aminium hexafluoroantimonate, FePhen: $[Fe(phen)_3](PF_6)_3$).

Substrate	Oxidation system	Yield (benzofuran)	Conversion (%)
1	200 mol% TNPA[a]	41% (**11**)	46
2	200 mol% TNPA[a]	19% (**11**)	26
3	200 mol% FePhen	70% (**11**)	69
4	200 mol% FePhen	46% (**11**)	100
5	200 mol% TNPA	64% (**12**)	66
5	Anode	58% (**12**)	100
6	400 mol% FePhen	72%[b] (**11**)	100
9	200 mol% FePhen	56% (**12**)	78

[a]In the presence of CH_3OH. [b]On a molar basis.

Discussion

The present investigations have led to the first characterization of phosphoenol radical cations in solution. For

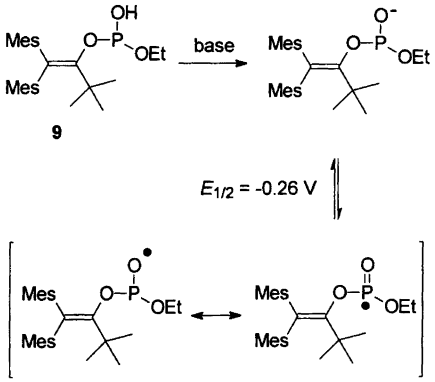
Table 7. g values of the EPR spectra of radical cations **1**$^{\bullet+}$–**3**$^{\bullet+}$.

	1$^{\bullet+}$	**2**$^{\bullet+}$	**3**$^{\bullet+}$
g	2.0015	2.0012	2.0019

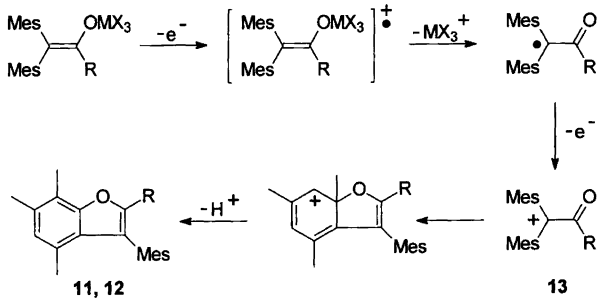
instance, EPR measurements at −100 °C allowed us to monitor directly the phosphoenol radical cations $\mathbf{1}^{\bullet+}$–$\mathbf{3}^{\bullet+}$ generated from the neutral precursors by oxidation with O_2AsF_6 in $CHClF_2$. Unfortunately, only unresolved spectra (for g values see Table 7) were obtained, preventing any structural discussion. Hence, for the present discussion the essential information about the phosphoenol radical cations was derived from the cyclic voltammetry investigations and preparative oxidations.

According to the oxidation potentials two distinct classes of phosphoenol electrophores can be identified: enol phosphite **4** and phosphoramidite **6** display rather low oxidation potentials (E_{pa} = 0.74 V and 0.60 V, respectively) whereas the enol phosphates **1**, **2** and **5** exhibit much higher anodic peak potentials in the range E_{pa} = 1.01 V–1.22 V. As compounds **4** and **6** carry a lone pair of electrons on the phosphorus atom it is legitimite to ask the question of whether the radical cations are of the enol type (C=C–O$^{\bullet+}$) or phosphane type ($PR_3^{\bullet+}$). To address this question we compared the half-wave potentials of **4** and **6** with those of simple phosphites. It turns out that the known potential of triethyl phosphite[20] [P(OEt)$_3$] $E^{ox}_{1/2}$ = 1.18 V_{Fc} is substantially higher than that of **4** ($E^{ox}_{1/2}$ = 0.86 V_{Fc}). This supports the assignment of $\mathbf{4}^{\bullet+}$ as an enol radical cation substituted with a moderately electron donating group [P(OR)$_2$]. On the other side, the oxidation potentials of enol phosphates are similar to those of enol acetates, e.g. $Mes_2C{=}C(Ph)OC(O)CH_3$ with E_{pa} = 1.04 V and $Mes_2C{=}C(^tBu)OC(O)CH_3$ with E_{pa} = 1.16 V, [10a] indicating that the acetyl and the phosphonoyl group have similar electron withdrawing properties. A change of the electrophore takes place by switching from **9** to the anion $\mathbf{9}^-$. The phosphite anion (Scheme 5) displays a reversible oxidation wave at $E_{1/2}$ = −0.26 V. Interestingly, the oxidation potential of methanolate (MeO^-) E^{ox} = −0.33 V_{Fc} is quite similar.[21]

In many in-depth-studies, the oxidative generation of the benzofuran moiety starting from various enols C=C–OMX_3 has been shown to proceed via the intermediacy of α-carbonyl cation **13** (Scheme 6). For instance, in the case of enol esters,[10a] silyl enol ethers,[10b] titanium



Scheme 5. Generation and subsequent oxidation of enol phosphite anion $\mathbf{9}^-$.

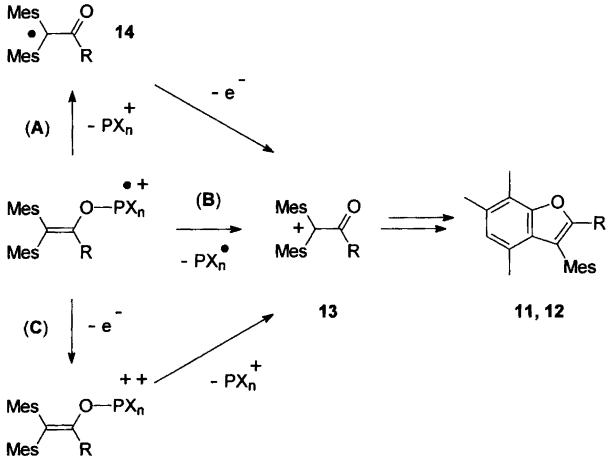


Scheme 6. Conversion of various enol derivatives (M = Si, Ti, Zr) via α-carbonyl cation **13** to the benzofurans **11**, **12**.

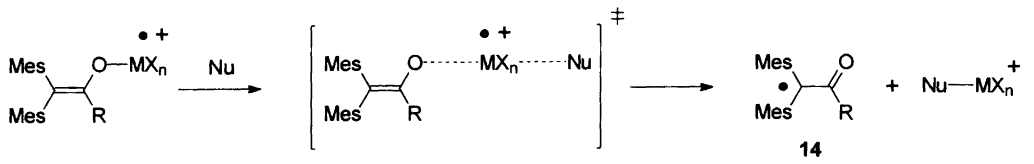
enolates[12] or enols themselves,[19] upon one-electron oxidation a mesolytic[22] M–O bond cleavage was inferred, which furnished the benzofurans **11** or **12** as stable end products.

In case of the phosphoenols investigated here the same stable end products and the same diagnostic criteria of the cyclic voltammograms are found as for the aforementioned enol derivatives. For instance, an ECE/DISP mechanism could be established because (i) the current function $i_{pa}v^{-1/2}$ decreases with increasing v and (ii) i_{pc}/i_{pa} increases from 0 to 1 with increasing v. In the course of the reaction two electrons are consumed, thus, a second electrochemical (E) step must be involved. Because of the analogy to the other enol derivatives, it is tempting to assign the chemical step following the initiating one-electron oxidation to a mesolytic P–O bond cleavage. However, with the phosphoenols the mechanistic scheme is somewhat more complex. Because of the relatively small difference, ΔE_c, of the first and the second oxidation step within the phosphoenols (Table 4) the following endergonic ET reaction may take place in solution (R: phosphoenol) eventually driven by the bond cleavage via mode **C** (see Scheme 7).

$$R^{\bullet+} + R^{\bullet+} \rightarrow R^{2+} + R$$



Scheme 7. Various mechanistic pathways for the conversion of phosphoenol radical cations into benzofurans via α-carbonyl cations.



Scheme 8. Nucleophile-induced M–O bond cleavage within enol radical cations.

As this ET pre-equilibrium is a bimolecular reaction, some simple diagnostic tests can be carried out. Indeed, the substrate concentration was found to influence the stability of the phosphoenol radical cations for $\mathbf{3}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ as probed by i_{pc}/i_{pa}. In these cases, reaction mode **C** may be involved to some extent. Nevertheless, the prevailing process is most likely a mesolytic P–O bond cleavage following either pathway **A** or **B** (Scheme 7), since CV investigations indicate that the phosphoenol dications are not that reactive. We have been able reversibly to oxidize $\mathbf{1}^{\bullet+}$ to its dication at fast scan rates (Fig. 2), indicating that the rate constants for fragmentation of dications such as $\mathbf{1}^{2+}$ are $k \approx 10^3\ s^{-1}$. In recent years, Olah[23] has shown that dications are stabilized significantly through conjugation to aryl groups, a situation which is found in the phosphoenols. Very recent results point to the fact that even structurally simple dications[24] or radical dications[25] may be generated, as well.

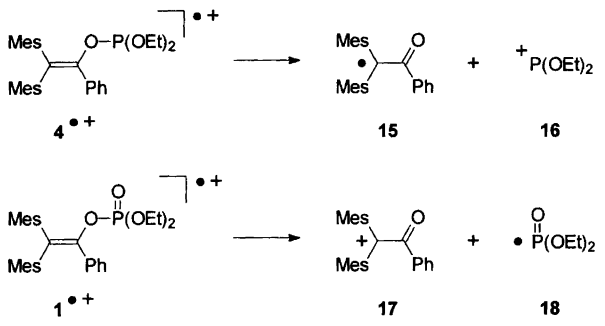
In earlier investigations conclusive evidence was presented[10b] that the scission mode **A** may be induced by nucleophiles, as in the case of silyl enol ethers. This is due to the ability of silicon to build up hypervalent structures,[26] which play an important role in the transition state of the nucleophile-induced bond cleavage (Scheme 8).

Similarly, phosphorus compounds are able to enlarge their coordination sphere,[27] so that a similar mechanism could, in principle, be active for M=P as well. Experimentally, a nucleophile-induced P–O bond cleavage has been found for the enol phosphite **4** but not for the enol phosphates **1**, **2** and **5** or the enol phosphinate **3**. Apparently, P–O bond cleavage in the enol phosphite radical cation $\mathbf{4}^{\bullet+}$ furnishes an α-carbonyl radical **15** and the phosphenium cation **16** (Scheme 9). Phosphenium ions have long been known as intermediates,[28] and some derivatives have even been isolated.[29] On the other hand, enol phosphates, such as **1**, most likely form α-carbonyl cations such as **17** and phosphonyl radicals **18** upon P–O bond scission.

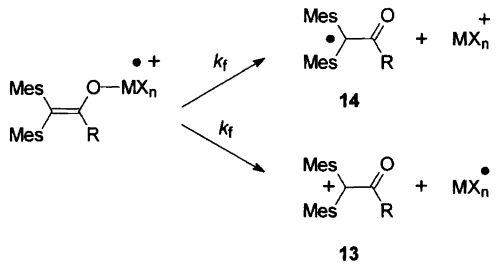
Because of the ECE/DISP mechanism, which has been found for all compounds **1**–**5**, it is clear that the radical fragments **15** and **18** are further oxidized in the CV experiment. Nevertheless, under PET conditions the mesolytic P–O bond cleavage of **1**–**3** and **5** could in principle be used selectively to generate phosphonyl radicals **18** which have been used for photoinitiation of polymerization processes.[30]

Altogether the kinetic results reveal a clear trend in the P–O bond cleavage rate constants: k (enol phosphate$^{\bullet+}$) < k (enol phosphinate$^{\bullet+}$) < k (enol phosphite$^{\bullet+}$). While all the enol phosphate radical cations exhibit very similar rate constants around $k \approx 1\ s^{-1}$, the P–O bond in the enol phosphite $\mathbf{4}^{\bullet+}$ is cleaved more rapidly by six orders of magnitude. At present, it is not fully clear why the presence of a P=O group should stabilize the P–O bond against mesolytic fragmentation. Some insight might be gained, however, from AM1 calculations[31] which indicate that the homolytic bond dissociation energy (BDE) of the P–O bond in $PO(OMe)_3$ is higher that that in $P(OMe)_3$ by about 20 kcal mol^{-1}. Assuming a similar BDE difference in the neutral enol phosphates as compared to the enol phosphite, one can derive, from simple thermochemical cycle calculations using the different enol oxidation potentials in Table 2, that for the mesolytic cleavage of **1**, **2**, $\mathbf{5}^{\bullet+}$ vs. $\mathbf{4}^{\bullet+}$ this difference should be reduced to about 11 kcal mol^{-1}. Hence, thermochemical cycle considerations indeed suggest that the P–O bond in the enol phosphite radical cation is easier to cleave than that in the enol phosphate radical cation in agreement with our kinetic results.

The rate constants k_f show that the enol phosphate radical cations $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$ and $\mathbf{5}^{\bullet+}$ [Scheme 10, MX_n=



Scheme 9. Postulated modes of bond cleavage within enol phosphite and enol phosphate radical cations.



Scheme 10. Mesolytic M–O bond cleavages within enol radical cations.

$P(O)(OEt)_2$, $P(O)(OPh)_2$] are more stable than silyl enol ether [$MX_n=SiR_3$], enol carbonate [$MX_n=C(O)OR$] and enol carbamate radical cations [$MX_n=C(O)NR_2$] because for these systems, k_f is higher than $600\ s^{-1}$ in acetonitrile.[10a,10b,32] Equally, titanium enolate radical cation $(Mes)_2C{=}C(H)OTiCp_2Cl^{\cdot+}$ with $k_f=850\ s^{-1}$ is more unstable than the enol phosphate radical cations.[12b] From the various compounds of the β,β-dimesitylethenol type studied hitherto, only trifluoroacetate radical cations have proved to fragment as slowly as the enol phosphate radical cations, e.g. $(Mes)_2C{=}C(t\text{-}Bu)OC(O)CF_3$ exhibiting $k_f=1.4\ s^{-1}$.[33]

In conclusion, we have prepared a series of phosphoenols and investigated their one-electron oxidation chemistry. Upon chemical or electrochemical oxidation, phosphoenol radical cations have been characterized for the first time in solution by cyclic voltammetry and EPR spectroscopy and an unprecedented P–O bond cleavage was established.

Experimental

General methods. All reactions were carried out under an atmosphere of nitrogen gas by using standard Schlenk tube techniques. Solvents were purified by standard literature methods and distilled directly from their drying agents under nitrogen: THF–potassium, acetonitrile–CaH_2, hexane–potassium, dichloromethane–P_4O_{10}. Solvents for CV measurements and one-electron oxidation experiments: acetonitrile was purchased in HPLC quality from Riedel-de-Haën, distilled from calcium hydride and filtered through basic alumina (ICN); dichloromethane was purchased in HPLC quality from Riedel-de-Haën, distilled from P_4O_{10} and filtered through basic alumina (ICN). Supporting electrolyte tetrabutylammonium hexafluorophosphate (Fluka) was of electrochemical grade and used without further purification. Methyl(phenyl)phosphinic acid chloride[34] and bis(diethylamino)chlorophosphane[35] were prepared as described in the literature. Diethyl chlorophosphate, diphenyl chlorophosphate and diethyl chlorophosphite were purchased from Fluka and were used as received. ^1H and ^{13}C NMR spectra were recorded on Bruker AC-200 and AM 250 instruments and calibrated with tetramethylsilane as an internal reference (TMS, $\delta=0.0$). IR spectra were recorded on a Perkin–Elmer 1605 series FT-IR spectrometer. Melting points were recorded on a Büchi melting point apparatus and are uncorrected. Elemental analyses were carried out on a Carlo Erba Elemental Analyzer 1106. Mass spectra were recorded on a Finnigan MAT-90 mass spectrometer under electronical ionization (EI; 70 eV) conditions.

(2,2-Dimesityl-1-phenylethenyl) diethyl phosphate (**1**). A solution of 2,2-dimesityl-1-phenylethenol (**7**) (0.40 g, 1.1 mmol) in anhydrous THF (5 ml) was slowly added to a suspension of NaH (27 mg, 1.1 mmol) in anhydrous THF (4 ml). The reaction mixture was stirred for 1 h, then diethyl chlorophosphate (0.20 ml, 0.24 g, 1.4 mmol) was added. The solution was heated to reflux for 19 h, after which it was evaporated and the product was purified by column chromatography (silica gel, diethyl ether–cyclohexane 2:1, R_f 0.53) yielding a pale yellow oil, which crystallized on standing. Recrystallization from acetonitrile furnished colorless rhombic crystals (180 mg, 0.37 mmol, 33%). M.p. 149–150 °C. IR (KBr): $\tilde{\nu}=2980\ cm^{-1}$ (s, C–H), 2918 (s, C–H), 1611 (m, C=C), 1560 (w, aryl), 1477 (m), 1442 (m), 1276 (s), 1042 (s), 972 (s), 861 (m), 695 (m). ^1H NMR (200 MHz, C_6D_6, 298 K): δ 1.01 (br s, 6 H, $OCH_2\underline{CH_3}$), 2.12 (s, 3 H, Mes-*p*-CH_3), 2.22 (s, 3 H, Mes-*p*-CH_3), 2.23–2.88 (m, 12 H, broadened through coalescence, Mes-*o*-CH_3), 3.55–4.10 (m, 4 H, broadened through coalescence, $O\underline{CH_2}CH_3$), 6.72 (s, 2 H, Mes-H), 6.86 (br s, 2 H, Mes-H), 6.99–7.15 (m, 3 H, Ph-H), 7.86–7.95 (m, 2 H, Ph-H). ^1H NMR (200 MHz, C_6D_6, 333 K): δ 1.05 (t, $J=7.1$ Hz, 6 H, $OCH_2\underline{CH_3}$), 2.13 (s, 3 H, Mes-*p*-CH_3), 2.24 (s, 3 H, Mes-*p*-CH_3), 2.38 (s, 6 H, Mes-*o*-CH_3), 2.51 (s, 6 H, Mes-*o*-CH_3), 3.53–3.89 (m, 4 H, $O\underline{CH_2}CH_3$), 6.73 (s, 2 H, Mes-H), 6.88 (s, 2 H, Mes-H), 6.99–7.15 (m, 3 H, Ph-H), 7.86–7.95 (m, 2 H, Ph-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 15.83 (Mes-CH_3), 15.99 (Mes-CH_3), 20.78 (Mes-CH_3), 20.87 (Mes-CH_3), 21.05 (Mes-CH_3), 28.69 (2 C, $OCH_2\underline{CH_3}$), 63.54 (d, $J_{P-C}=7.0$ Hz, 2 C, $O\underline{CH_2}CH_3$), 127.10, 127.22, 127.61, 128.28, 128.92 (br s), 129.31, 129.46, 134.56, 134.86, 134.92, 136.47, 136.56, 138.29, 139.01, 146.14 (C=C–O). ^{31}P NMR (162 MHz, $CDCl_3$): δ −5.67 (s). MS-EI: *m/z* (% rel. int.) 492 (M^+, 14), 356 (65), 341 (27), 338 (27), 323 (20), 313 (17), 251 (17), 219 (10), 178 (11), 127 (66), 125 (12), 111 (29), 105 (18), 99 (100), 82 (36), 81 (35). Analysis: calc. for $C_{30}H_{37}O_4P$: C, 73.15; H, 7.57%. Found: C, 72.84; H, 7.25%.

(2,2-Dimesityl-1-phenylethenyl) diphenyl phosphate (**2**). A suspension of KH (40 mg, 1.0 mmol) in anhydrous THF (4 ml) was treated with a solution of **7** (0.36 g 1.0 mmol) in anhydrous THF (3 ml). The reaction mixture was stirred for 1 h at room temp., then diphenyl chlorophosphate (0.25 ml, 0.32 g, 1.2 mmol) was added by syringe. After the solution had been allowed to reflux for 3 d the solvent was evaporated off and the residue was purified by chromatography (silica gel; *n*-hexane–diethyl ether 2:1, R_f 0.41). 260 mg (0.44 mmol, 44%) of colorless crystals were obtained. M.p. 151–153 °C. IR (KBr): $\tilde{\nu}=2917\ cm^{-1}$ (m, C–H), 1591 (m, C=C), 1560 (w, aryl), 1491 (s), 1456 (m), 1300 (m), 1218 (s), 1194 (s), 1051 (s), 1025 (s), 976 (s), 947 (s), 751 (m), 688 (m), 502 (m). ^1H NMR (200 MHz, C_6D_6, 298 K): δ 2.11 (s, 6 H, Mes-CH_3), 2.24–2.83 (br s, 12 H, Mes-CH_3), 6.71 (s, 2 H, Mes-H), 6.76 (br s, 2 H, Mes-H), 6.85–6.89 (m, 2 H, Ph-H), 6.94–7.05 (m, 7 H, Ph-H), 7.15–7.27 (m, 4 H, Ph-H), 7.75–7.83 (m, 2 H, Ph-H). ^1H NMR (200 MHz, C_6D_6, 333 K): δ 2.13 (s, 6 H, Mes-CH_3), 2.37 (s, 6 H, Mes-CH_3), 2.50 (s, 6 H, Mes-CH_3), 6.73 (s, 2 H, Mes-H), 6.78 (s, 2 H, Mes-H), 6.82–6.92 (m, 2 H,

Ph-H), 6.98–7.05 (m, 6 H, Ph-H), 7.14–7.24 (m, 5 H, Ph-H), 7.75–7.83 (m, 2 H, Ph-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.81 (Mes-CH_3), 21.08 (Mes-CH_3), 21.35 (Mes-CH_3), 119.82, 119.94, 124.88, 127.64, 127.73, 127.89, 128.01, 128.25, 128.49, 128.67, 129.13, 129.37, 130.40, 133.86, 134.62, 135.74, 136.74, 138.23, 138.77, 146.17 (C=C–O), 150.59 (d, J_{P-C} = 7.5 Hz, 2 C, OPh, C-1). ^{31}P NMR (162 MHz, $CDCl_3$): δ −15.94 (s). Analysis: calc. for $C_{38}H_{37}O_4P$: C, 77.53; H, 6.34%. Found: C, 77.48; H, 6.10%.

(2,2-Dimesityl-1-phenylethenyl) methyl phenyl phosphinate (**3**). A suspension of NaH (40 mg, 1.7 mmol) in anhydrous THF (4 ml) was treated with a solution of **7** (0.61 g, 1.7 mmol) in anhydrous THF (5 ml). The reaction mixture was allowed to stir at room temp. for 1 h. A solution of methylphenylphosphinic acid chloride[34] (0.44 g, 2.5 mmol) in anhydrous THF (3 ml) was then added. The solution was refluxed overnight after which the solvent was evaporated off *in vacuo*. The product was purified by chromatography (silica gel; diethyl ether, R_f 0.63) yielding a colorless oil which crystallized on standing. After recrystallization from *n*-pentane 240 mg (0.49 mmol, 29%) of colorless crystals were obtained. M.p. 177–179 °C. IR (KBr): $\tilde{\nu}$ = 2916 cm^{-1} (m, C–H), 1609 (m, C=C), 1560 (w, aryl), 1439 (m), 1302 (m), 1233 (s), 1123 (s), 1054 (s), 1024 (m), 921 (m), 889 (s), 851 (m), 810 (m), 774 (m), 740 (s), 694 (s), 506 (m), 460 (m). ^{1}H NMR (200 MHz, C_6D_6, 298 K): δ 0.86 (br s, 3 H, PCH_3), 2.03–2.85 (m, 18 H, Mes-CH_3), 6.70 (s, 2 H, Mes-H), 6.74 (s, 2 H, Mes-H), 6.75–7.22 (m, 6 H, Ph-H), 7.55 (br s, 2 H, Ph-H), 7.92 (br s, 2 H, Ph-H); several signals are broadened because of coalescence. ^{1}H NMR (200 MHz, C_6D_6, 333 K): δ 1.09 (d, J_{P-H} = 14.4 Hz, 3 H, PCH_3), 2.13 (s, 3 H, Mes-CH_3), 2.20 (s, 3 H, Mes-CH_3), 2.33 (s, 3 H, Mes-CH_3), 2.41 (s, 3 H, Mes-CH_3), 2.44 (s, 3 H, Mes-CH_3), 2.59 (s, 3 H, Mes-CH_3), 6.72 (s, 2 H, Mes-H), 6.75 (s, 2 H, Mes-H), 6.84–7.19 (m, 6 H, Ph-H), 7.50–7.67 (m, 2 H, Ph-H), 7.69–7.88 (m, 2 H, Ph-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 20.66, 20.87, 21.06, 21.42, 126.94, 127.49, 128.03, 128.15, 128.33, 128.67, 129.21, 129.30, 129.79, 130.25, 130.46, 131.55, 135.07, 136.46, 136.86, 138.83, 146.65 (C=C–O). ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.04 (s). Analysis: calc. for $C_{33}H_{35}O_2P$: C, 80.14; H, 7.13%. Found: C, 79.90; H 6.97%.

1-Diethoxyphosphinoxy-2,2-dimesityl-1-phenylethene (**4**). Triethylamine (0.84 ml, 0.60 g, 6.0 mmol) was added to a solution of **7** (1.6 g, 4.5 mmol) in acetonitrile (18 ml) and dichloromethane (18 ml). After being stirred for 5 min at room temp., the solution was treated with diethyl chlorophosphite (0.85 ml, 0.94 g, 6.0 mmol) and refluxed for 16 h. The reaction mixture was cooled in an ice bath and treated with cold dichloromethane (40 ml) and cold saturated $NaHCO_3$ solution (40 ml). The layers were separated and the organic layer was dried over $CaCl_2$. After removal of the solvent the product was isolated by column chromatography (neutral Al_2O_3; *n*-hexane–diethylether 4:1, R_f 0.71) providing 740 mg (1.6 mmol, 35%) of colorless crystals. M.p. 127–128 °C. IR (KBr): $\tilde{\nu}$ = 2976 cm^{-1} (m, C–H), 2918 (m, C–H), 1610 (m, C=C), 1441 (m), 1238 (m), 1021 (s, P–O–aryl), 903 (s), 754 (s). ^{1}H NMR (200 MHz, $CDCl_3$, 298 K): δ 1.14 (br s, 6 H, OCH_2CH_3), 1.80–2.50 (2 br s, 6 H, Mes-CH_3), 2.18 (s, 3 H, Mes-CH_3), 2.25 (s, 3 H, Mes-CH_3), 3.30–4.10 (2 br s, 4 H, OCH_2), 6.65 (s, 2 H, Mes-H), 6.79 (br s, 2 H, Mes-H), 7.11–7.14 (m, 3 H, Ph-H), 7.36–7.41 (m, 2 H, Ph-H); several signals are broadened because of coalescence. ^{1}H NMR (200 MHz, DMSO, 373 K): δ 1.19 (t, J = 7.0 Hz, 6 H, OCH_2CH_3), 2.03 (s, 6 H, Mes-CH_3), 2.18 (s, 6 H, Mes-CH_3), 2.23 (s, 3 H, Mes-CH_3), 2.31 (s, 3 H, Mes-CH_3), 3.72 (q, J = 7.0 Hz, 4 H, OCH_2), 6.75 (s, 2 H, Mes-H), 6.89 (s, 2 H, Mes-H), 7.23–7.26 (m, 3 H, Ph-H), 7.40–7.44 (m, 2 H, Ph-H). ^{13}C NMR (50 MHz, $CDCl_3$, TMS): δ 16.59 (OCH_2CH_3), 16.68 (OCH_2CH_3), 20.78, 20.84, 21.05, 58.02 (OCH_2), 58.26 (OCH_2), 123.34 (C=C–O), 127.43, 127.92, 129.31, 135.68, 135.86, 136.16, 137.95, 139.08, 148.54 (C=C–O). ^{31}P NMR (162 MHz, $CDCl_3$, TMS): δ 139.42 (s). Analysis: calc. for $C_{30}H_5$-O_3P: C, 75.61; H, 7.83%. Found: C, 75.71; H, 8.06%.

(1,1-Dimesityl-3,3-dimethylbut-1-en-2-yl) diethyl phosphate (**5**). A suspension of NaH (60 mg, 2.5 mmol) in anhydrous THF (4 ml) was treated with a solution of 1,1-dimesityl-3,3-dimethylbut-1-en-2-ol (**8**) (0.84 g, 2.5 mmol) in anhydrous THF (5 ml). The reaction mixture was stirred for 1 h at room temp., then diethyl chlorophosphate (0.43 ml, 0.52 g, 3.0 mmol) was added and the mixture was refluxed overnight. After cooling to room temp. dichloromethane (15 ml) was added and the solution was extracted with a cold saturated aqueous solution of $NaHCO_3$ (20 ml). The layers were separated and the organic layer was dried over $MgSO_4$. After removal of the solvent *in vacuo* the residue was subjected to column chromatography (silica gel; dichloromethane, R_f 0.22). The product was obtained as colorless oil. Yield: 530 mg (1.1 mmol, 44%). IR (neat): $\tilde{\nu}$ = 2962 cm^{-1} (s, C–H), 1610 (m, C=C), 1564 (w, aryl), 1478 (s), 1396 (m), 1275 (m), 1129 (w), 1025 (s), 976 (m), 852 (w). ^{1}H NMR (200 MHz, C_6D_6, 298 K): δ 1.01 (br s, 6 H, OCH_2CH_3), 1.36 [s, 9 H, $C(CH_3)_3$], 2.02–2.25 (m, 3 H, Mes-CH_3), 2.19 (s, 6 H, Mes-CH_3), 2.40–2.73 (m, 6 H, Mes-CH_3), 3.03 (br s, 3 H, Mes-CH_3), 3.90 (br s, 4 H, OCH_2CH_3), 6.71–6.89 (m, 4 H, Mes-H); several signals are broadened because of coalescence. ^{1}H NMR (200 MHz, C_6D_6, 333 K): δ 1.06 (dt, J_{H-H} = 7.5 Hz, J_{H-P} = 1.1 Hz, 6 H, OCH_2CH_3), 1.37 [s, 9 H, $C(CH_3)_3$], 2.22 (s, 6 H, Mes-*p*-CH_3), 2.53 (br s, 12 H, Mes-*o*-CH_3), 3.53–3.79 (m, 4 H, OCH_2CH_3), 6.82 (s, 2 H, Mes-H), 6.85 (s, 2 H, Mes-H). ^{13}C NMR (50 MHz, C_6D_6): δ 15.92 (Mes-CH_3), 16.07 (Mes-CH_3), 20.62 (Mes-CH_3), 20.80 (Mes-CH_3), 21.83 (br, Mes-CH_3), 29.20 [5 C, OCH_2CH_3 and $C(CH_3)_3$], 39.66 [$C(CH_3)_3$], 62.85 (d, J_{P-C} = 4.5 Hz, 2 C, OCH_2CH_3), 125.21, 125.33,

127.51–128.49 (signals obscured by solvent signals), 135.80, 135.92, 136.42, 136.63, 139.83, 153.29 (C=C–O). MS-EI: *m/z* (% rel. int.) 472 (M^+, 32), 303 (54), 262 (100), 261 (40), 251 (50), 249 (15), 247 (29), 246 (24), 155 (11), 132 (28), 126 (20), 119 (12), 99 (26), 81 (11), 57 (38). HRMS: calc. for $C_{28}H_{41}O_4P$: 472.2742. Found: 472.2748.

Diethylamino[bis(2,2-dimesityl-1-phenylethenoxy)]-λ^3-phosphane (**6**). A solution of **7** (1.0 g, 2.8 mmol) in dichloromethane (10 ml) and acetonitrile (10 ml) was treated first with triethylamine (0.52 ml, 0.38 g, 3.8 mmol) and then with bis(diethylamino)chlorophosphane[35] (0.41 g, 2.0 mmol). The solution was refluxed for 24 h during which time the color changed from dark brown to orange–brown. The solvent was then removed *in vacuo* and the residue was dissolved in dichloromethane (5 ml). The product was isolated by column chromatography (neutral Al_2O_3; *n*-hexane–dichloromethane 4:1, R_f 0.78) furnishing 390 mg (0.48 mmol, 34%) of colorless crystals. M.p. 178–182 °C (decomp.). IR (KBr): $\tilde{\nu}=2919\ cm^{-1}$ (s, C–H), 1608 (m, C=C), 1558 (m), 1444 (s), 1230 (m), 1193 (m), 1136 (m), 1019 (s, P–O–Aryl), 903 (m), 849 (m), 744 (m), 691 (s). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 0.73 (t, J= 7.3 Hz, 6 H, NCH_2CH_3), 1.91 (s, 6 H, Mes-CH_3), 1.93 (s, 6 H, Mes-CH_3), 1.95 (br s, 6 H, Mes-CH_3), 2.14 (s, 6 H, Mes-CH_3), 2.21 (s, 6 H, Mes-CH_3), 2.23 (br s, 6 H, Mes-CH_3), 2.32 (q, J=7.3 Hz, 4 H, NCH_2), 6.58 (s, 2 H, Mes-H), 6.60 (s, 2 H, Mes-H), 6.68 (s, 2 H, Mes-H), 6.76 (s, 2 H, Mes-H), 6.99–7.10 (m, 6 H, Ph-H), 7.42 (m, 4 H, Ph-H), several signals are broadened because of coalescence. ^{13}C NMR (50 MHz, $CDCl_3$, TMS): δ 14.23 (NCH_2CH_3), 14.36 (NCH_2CH_3), 20.73, 20.78, 21.15, 21.33, 21.66, 22.03 (each one Mes-CH_3), 37.43 (NCH_2), 37.92 (NCH_2), 127.06 (C=C–O), 127.58, 128.82, 128.91, 129.15, 129.24, 130.06, 135.61, 135.79, 136.64, 137.83, 138.01, 138.37, 138.64, 139.01, 150.20 (C=C–O). ^{31}P NMR (162 MHz, $CDCl_3$, TMS): δ 143.12 (s). MS-ESI: *m/z* (% rel. int.) 814 ($M+1$, 100), 741 ($M-NEt_2$, 40), 355 ($OPhC{=}CMes_2$, 30), 339 ($Mes_2C{=}CPh$, 40). Analysis: calc. for $C_{56}H_{64}NO_2P$: C, 82.61; H, 7.93%; N 1.72%. Found: C, 81.98; H, 8.16; N, 1.73%.

(1,1-Dimesityl-3,3-dimethylbut-1-en-2-yl) ethyl phosphite (**9**). A solution of **8** (0.88 g, 2.6 mmol) in anhydrous THF (4 ml) was added to a suspension of NaH (63 mg, 2.6 mmol) in anhydrous THF (6 ml). The reaction mixture was stirred for 1 h at room temp. and then treated with diethyl chlorophosphite (0.50 ml, 0.55 g, 3.5 mmol). The mixture was refluxed overnight after which the solvent was evaporated off and the residue subjected to column chromatography (silica gel; dichloromethane, R_f 0.56). A colorless oil was obtained which crystallized on standing. Yield: 240 mg (0.60 mmol, 22%) of colorless crystals. M.p. 101–103 °C. IR (KBr): $\tilde{\nu}=3431\ cm^{-1}$ (br s, O–H), 2966 (s, C–H), 2918 (s, C–H), 2460 (m, P–H), 1610 (m, C=C), 1560 (w, aryl), 1475 (m), 1258 (s), 1071 (m), 955 (s), 853 (m), 530 (m). ^1H NMR (200 MHz, C_6D_6, 298 K): δ 0.34 (t, J=7.1 Hz, 3 H, OCH_2CH_3), 0.65 [s, 9 H, $C(CH_3)_3$], 1.38–1.60 (m, 9 H, Mes-CH_3), 1.71–2.02 (m, 6 H, Mes-CH_3), 2.36 (br s, 3 H, Mes-CH_3), 3.14 (br s, 2 H, OCH_2CH_3), 6.08–6.27 (m, 4 H, Mes-H). ^1H NMR (200 MHz, C_6D_6, 333 K): δ 0.41 (t, J=7.9 Hz, 3 H, OCH_2CH_3), 0.65 [s, 9 H, $C(CH_3)_3$], 1.56 (s, 3 H, Mes-CH_3), 1.57 (s, 3 H, Mes-CH_3), 1.64 (s, 3 H, Mes-CH_3), 1.74 (s, 3 H, Mes-CH_3), 1.90 (s, 3 H, Mes-CH_3), 2.09 (s, 3 H, Mes-CH_3), 3.06–3.21 (m, 2 H, OCH_2), 3.69 (s, 1 H, OH), 6.11 (s, 1 H, Mes-H), 6.16 (s, 1 H, Mes-H), 6.22 (s, 1 H, Mes-H), 6.25 (s, 1 H, Mes-H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 16.17, 16.29, 20.69, 20.78, 21.11, 21.38, 22.11 (br s), 28.66 (OCH_2CH_3), 39.00 [$C(CH_3)_3$], 61.14 (d, J_{P-C}= 6.0 Hz, 1 C, OCH_2), 128.10, 128.73, 129.16, 130.37, 134.31, 135.01, 136.41, 136.77, 138.92, 139.29, 153.05, 153.30. ^{31}P NMR (162 MHz, $CDCl_3$): δ 2.81 (s). MS-EI: *m/z* (% rel. int.) 428 (M^+, 39), 303 (50), 263 (23), 262 (100), 261 (40), 247 (35), 246 (25). Analysis: calc. for $C_{26}H_{37}O_3P$: C, 72.87; H, 8.70%. Found: C, 72.59; H, 8.69%.

General procedure for one-electron oxidations. In an argon-filled glovebox the desired amounts of the one-electron oxidant (FePhen or TNPA) and the phosphoenol were placed into two separate test tubes equipped with stirring rods. On a high purity argon line, acetonitrile (3 ml) was added to each test tube to dissolve the reactants. The substrate solution was added by means of a syringe to the solution of the one-electron oxidant. The resulting mixture was stirred at room temp. for 14 h, quenched with saturated aqueous $NaHCO_3$ (10 ml) and diluted with dichloromethane (10 ml). The aqueous layer was extracted three times with dichloromethane and the combined organic layers were washed with water. The solution was dried over Na_2SO_4 and the solvent was removed *in vacuo*. If FePhen was used as the oxidant the residue was treated with diethyl ether in order to remove $[Fe(phen)_3](PF_6)_2$ which precipitates as a red solid. The product mixture was analyzed by ^1H NMR spectroscopy. All products were identified by comparison with data of authentic samples. Yields were determined by addition of *m*-nitroacetophenone as an internal ^1H NMR standard.

Anodic oxidation of **5**. Enol phosphate **5** (20 mg, 0.043 mmol) was dissolved in anhydrous acetonitrile (3 ml) containing 0.1 M tetrabutylammonium hexafluorophosphate. In an undivided electrochemical cell the solution was electrolyzed by applying a potential of 1.7 V vs. Ag with vigorously stirring of the solution. Platinum wires were used as working and counter electrode and an Ag-wire was used as the reference electrode. After 2 h, analysis by thin layer chromatography indicated that conversion of the reactant was complete. The brown solution was treated with dichloromethane

(10 ml) and water (20 ml). The layers were separated, the aqueous layer was extracted three times with dichloromethane (portions of 20 ml) and the combined organic layers were washed with water (30 ml). The solution was dried over $CaCl_2$ and the solvent was removed *in vacuo*. In order to get rid of the supporting electrolyte the residue was dissolved in diethyl ether (5 ml) and filtered through a short column of silica gel. The product mixture was analyzed by ^1H NMR spectroscopy.

Data for 3-mesityl-2-phenyl-4,6,7-trimethylbenzo[b]furan (**11**).[10b] ^1H NMR (250 MHz, $CDCl_3$) δ 1.89 (s, 3 H, *p*-Mes-CH_3), 2.02 (s, 6 H, *o*-Mes-CH_3), 2.39 and 2.40 (two s, each 3 H, 4- and 6-CH_3), 2.54 (s, 3 H, 7-CH_3), 6.76 (s, 1 H, 5-H), 6.98 (s, 2 H, Mes-H), 7.17–7.30 (m, 3 H, Ph-H), 7.48–7.55 (m, 2 H, Ph-H).

Data for 2-tert-butyl-3-mesityl-4,6,7-trimethylbenzo[b]furan (**12**).[36] ^1H NMR (250 MHz, $CDCl_3$): δ 1.20 [s, 9 H, $C(CH_3)_3$], 1.71 (s, 3 H, Mes-*p*-CH_3), 2.03 (s, 6 H, Mes-*o*-CH_3), 2.31 and 2.32 (two s, each 3 H, 4-CH_3 and 6-CH_3), 2.41 (s, 3 H, 7-CH_3), 6.65 (s, 1 H, 5-H), 6.87 (s, 2 H, Mes-H).

Cyclic voltammetry. In a glove box tetrabutylammonium hexafluorophosphate (232 mg, 600 μmol) and the substrate (6 μmol) were placed in a thoroughly dried CV cell. On a high purity argon line acetonitrile or dichloromethane (6 ml) was added by means of a gas-tight syringe. A platinum disc working electrode (diameter: 1 mm), a platinum wire counter electrode and a silver wire as pseudo-reference electrode were then placed in the solution. The cyclic voltammograms were recorded at various scan rates using different starting and switching potentials. For determination of the oxidation potentials, ferrocene ($E_{1/2} = +0.39$ V vs. SCE) was added as an internal standard. Cyclic voltammograms were recorded using a Princeton Applied Research model 362 potentiostat with a Philips model PM 8271 XYt-recorder for scan rates $< 1\ V\ s^{-1}$. For fast scan cyclic voltammetry, a Hewlett Packard model 3314A function generator was used connected to a three-electrode potentiostat developed by Amatore.[37] The working electrodes were self-made gold (diameter: 25 μm) and platinum (diameter: 10 μm) ultramicroelectrodes.

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