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.


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 \( \text{P(OEt)}_2 \) (16) and \( \text{P(=O)(OEt)}_2 \) (18) can be generated selectively by mesolytic cleavage. At high scan rates, the partially reversible oxidation wave \( 1^{+} \rightleftharpoons 1^{++} \) 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 and since they undergo synthetically helpful cross-coupling reactions with C–C bond formation. 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, enol phosphates have received far less attention.

With regard to electron transfer activation only the one-electron reduction of enol phosphates has been investigated 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 which have been shown to be important intermediates in the \( \alpha \)-umpolung of ketones and aldehydes, in diastereoselective carbon–carbon bond formation and in the synthesis of benzofurans. Since many enol functionalities, among which we should quote silyl enol ethers, tin enolates, and titanium enolates, 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. To facilitate the characterization of the radical cations we have used bulky \( \beta \beta \)-dimethyl enols as precursors, since the crowded aryl groups exert steric hindrance about the \( \beta \)-carbon in the enol derivative which is doubly helpful: (a) nucleophiles cannot attack at the \( \beta \)-carbon and (b) dimerization at the \( \beta \)-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 \( \alpha \)-bromo ketones with trialkyl phosphites; however, the above model compounds were prepared from the enolates and the appropriate phosphoryl chlorides (Scheme 2 and
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-dimethyl-1-phenylethenol (7) and 1,1-dimethyl-3,3-dimethylene-1-en-2-ol (8), were used as the starting materials. Remarkably, after reacting enol 8 with NaH and chlorodiethylphosphite in THF enol phosphite 9 was isolated with a deficiency of one ethoxy group and carrying a hydroxy group instead (Scheme 3).

Biseno phosphoramidite 6 was synthesized in 34% yield by reacting two equivalents of the enolate of 7 with one equivalent of CIP(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 (see Table 2) the various phosphoenols were investigated by cyclic voltammetry in acetonitrile. At a scan rate $v = 100$ mV s$^{-1}$ only irreversible oxidation 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 phosphonate which can also be oxidized electrochemically by means of cyclic voltammetry. After treatment of 9 with 100 mol% of (Me$_4$N)OH as base: $E^{\text{1/2}}_{1/2} = -0.26$ V.

**Cyclic voltammetry (CV).** The CV diagnostics 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) $i_{pa}/v$ 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).

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

### 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{pa}$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.01</td>
</tr>
<tr>
<td>2</td>
<td>1.10</td>
</tr>
<tr>
<td>3</td>
<td>0.97</td>
</tr>
<tr>
<td>4</td>
<td>0.74$^a$</td>
</tr>
</tbody>
</table>

$^aE^{\text{1/2}}_{1/2} = 0.86$ V in dichloromethane. $^b$In the presence of 100 mol% (Me$_4$N)OH as base: $E^{\text{1/2}}_{1/2} = -0.26$ V.

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

<table>
<thead>
<tr>
<th>Enol</th>
<th>$i_{pa}$/mA</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>2.0</td>
</tr>
<tr>
<td>1</td>
<td>1.8</td>
</tr>
<tr>
<td>2</td>
<td>1.7</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
</tr>
<tr>
<td>4</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Ref. $i_{pa} = 2.0$.
was determined at 100 mV s⁻¹.²²

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 phosphonols exhibit reduction waves only at higher scan rates, e.g. enol phosphate 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 irreversible, 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 iₚc/iₚn. Of the phosphonols 1–5, only the oxidation waves of enol phosphate 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 phosphate 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 kᵣ of the follow-up reaction could be derived (Table 5). This rate constant kᵣ 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 1⁺, 2⁺ and 5⁺ is about 0.04 to 0.2 s⁻¹ in dichloromethane, which is lower than that of enol phosphate 3⁺ and again much lower than the rate of enol phosphate 4⁺. 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 kᵣ > 10⁵ 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 4. ΔEₑ = Eₑ₂ (second wave) – Eₑ₁ (first wave): difference of potential between the first and the second oxidation step in phosphonols 1–5, as determined at 100 mV s⁻¹.²²

<table>
<thead>
<tr>
<th></th>
<th>ΔEₑ (1)/mV</th>
<th>ΔEₑ (2)/mV</th>
<th>ΔEₑ (3)/mV</th>
<th>ΔEₑ (4)/mV</th>
<th>ΔEₑ (5)/mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>In CH₃CN</td>
<td>180*</td>
<td>190*</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>In CH₂Cl₂</td>
<td>230</td>
<td>180</td>
<td>200</td>
<td>200</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

* Determined at 1.0 V s⁻¹. ¹¹ Not determined. ²² Determined at 8000 V s⁻¹.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Dichloromethane</th>
<th>Acetonitrile</th>
</tr>
</thead>
<tbody>
<tr>
<td>1⁺</td>
<td>3.9 x 10⁻²</td>
<td>9.0 x 10⁻¹</td>
</tr>
<tr>
<td>2⁺</td>
<td>5.0 x 10⁻²</td>
<td>7.0 x 10⁻¹</td>
</tr>
<tr>
<td>3⁺</td>
<td>5.0 x 10⁻¹</td>
<td>5.8 x 10⁴</td>
</tr>
<tr>
<td>4⁺</td>
<td>1.0 x 10⁴</td>
<td>&gt; 10⁶</td>
</tr>
<tr>
<td>5⁺</td>
<td>0.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* iₚc/iₚn is slightly susceptible to substrate concentration, see the text.

Fig. 1. Multiple sweep CV experiment with compound 9 (acetonitrile, 100 mV s⁻¹).

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substrate concentration. For compounds 3 ($k_r = 5.0 \times 10^{-1} \text{s}^{-1}$ for $c = 6.6 \times 10^{-4} \text{M}$; $k_r = 8.5 \times 10^{-1} \text{s}^{-1}$ for $c = 2.2 \times 10^{-3} \text{M}$) and 5 ($k_r = 2.0 \times 10^{-1} \text{s}^{-1}$ for $c = 6.3 \times 10^{-4} \text{M}$; $k_r = 2.4 \times 10^{-1} \text{s}^{-1}$ for $c = 2.2 \times 10^{-3} \text{M}$) 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 phosphenols, the EPR spectra of compounds $1^{+*}, 3^{+*}$ were recorded. To this end, the radical cations were generated through oxidation with O$_2$AsF$_6$ in CHClF$_2$ ($-100^\circ\text{C}$) but only unresolved spectra could be obtained (for $g$ values see Table 7).

\begin{table}[h]
\centering
\begin{tabular}{ccc}
\hline
Substrate & Oxidation system & Yield (benzofuran) \% & Conversion \%
\hline
1 & 200 mol% TNPA* & 41 (11) & 46
2 & 200 mol% TNPA* & 19 (11) & 26
3 & 200 mol% FePhen & 70 (11) & 69
4 & 200 mol% FePhen & 46 (11) & 100
5 & 200 mol% TNPA & 64 (12) & 66
6 & Anode & 58 (12) & 100
7 & 400 mol% FePhen & 72 (6) & 100
8 & 200 mol% FePhen & 56 (12) & 78
\hline
\end{tabular}
\caption{Yields of benzofurans in the oxidation of phosphenols (reaction in acetonitrile at room temp.; TNPA: tris(p-nitrophenyl)aminium hexafluorosantimonate; FePhen: \{Fe(phen)$_3$\}(PF$_6$)$_3$).
}
\end{table}

*a in the presence of CH$_3$OH. *b On a molar basis.

Discussion

The present investigations have led to the first characterization of phosphenol radical cations in solution. For $g$ values see Table 7.

\begin{table}[h]
\centering
\begin{tabular}{ccc}
\hline
 & $1^{+*}$ & $2^{+*}$ & $3^{+}$
\hline
$g$ & 2.0015 & 2.0012 & 2.0019
\hline
\end{tabular}
\caption{g values of the EPR spectra of radical cations $1^{+*}, 2^{+*}, 3^{+}$.
}
\end{table}
instance, EPR measurements at −100 °C allowed us to monitor directly the phosphoenol radical cations $1^{+}\cdot 3^{+}$ generated from the neutral precursors by oxidation with O$_2$AsF$_5$ 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 electrophiles can be identified: enol phosphite 4 and phosphoramidite 6 display rather low oxidation potentials ($E_{pa} = 0.74 \mathrm{V}$ and 0.60 V, respectively) whereas the enol phosphates 1, 2 and 5 exhibit much higher anodic peak potentials in the range $E_{pa} = 1.01 \mathrm{V} - 1.22 \mathrm{V}$. As compounds 4 and 6 carry a lone pair of electrons on the phosphorus atom it is legitimate to ask the question of whether the radical cations are of the enol type (C=−C=O $^+$) or phosphate type (PR$_3$$^+$). To address this question we compared the half-wave potentials of 4 and 6 with those of simple phosphites. It turns out that the known potential of triethyl phosphate$^{20}$ [P(OEt)$_3$] $E^{1/2}_{1/2}$ = 1.18 V$_{fc}$ is substantially higher than that of 4 ($E^{1/2}_{1/2}$ = 0.86 V$_{fc}$). This supports the assignment of 4$^{+}$ as an enol radical cation substituted with a moderately electron donating group [P(OEt)$_3$]. On the other side, the oxidation potentials of enol phosphates are similar to those of enol acetates, e.g. Mes$_2$C=C(Ph)OCC(O)CH$_3$ with $E_{pa} = 1.04 \mathrm{V}$ and Mes$_2$C=C(Bu)OC(O)CH$_3$ with $E_{pa} = 1.16 \mathrm{V}$, indicating that the acetyl and the phosphonyl group have similar electron withdrawing properties. A change of the electrophore takes place by switching from 9 to the anion 9$^-$. The phosphate anion (Scheme 5) displays a reversible oxidation wave at $E_{1/2} = -0.26 \mathrm{V}$. Interestingly, the oxidation potential of methanolate (MeO$^-$) $E^{ox} = -0.33 \mathrm{V}_{fc}$ 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 intermediary of α-carbonyl cation 13 (Scheme 6). For instance, in the case of enol esters,$^{10a}$ silyl enol ethers,$^{10b}$ titanium

![Scheme 6](image)

**Scheme 6.** Conversion of various enol derivatives (M=S, 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 $I_{an} = V^{1/2}$ decreases with increasing $V$ and (ii) $I_{pa}/I_{an}$ 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 mechanism scheme is somewhat more complex. Because of the relatively small difference, $\Delta E_{c}$, 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).

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

![Scheme 7](image)

**Scheme 7.** Various mechanistic pathways for the conversion of phosphoenol radical cations into benzofurans via α-carbonyl 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 3' + and 5' + as probed by $f_{nu}/f_{nu}$. 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 dication are not that reactive. However, we have been able reversibly to oxidize 1' + to its dication at fast scan rates (Fig. 2), indicating that the rate constants for fragmentation of dications such as 1' + are $k \approx 10^5 \text{s}^{-1}$. In recent years, Ohlah 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 or radical dications may be generated, as well.

In earlier investigations conclusive evidence was presented 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, 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, 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, 3. Apparently, P–O bond cleavage in the enol phosphite radical cation 4' + furnishes an $\alpha$-carbonyl radical 15 and the phosphonium cation 16 (Scheme 9). Phosphonium ions have long been known as intermediates, and some derivatives have even been isolated. On the other hand, enol phosphates, such as 1, most likely form $\alpha$-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.

Altogether the kinetic results reveal a clear trend in the P–O bond cleavage rate constants: $k$ (enol phosphate') $<$ $k$ (enol phosphinate') $<$ $k$ (enol phosphite'). While all the enol phosphate radical cations exhibit very similar rate constants around $k \approx 1 \text{s}^{-1}$, the P–O bond in the enol phosphite 4' + 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 which indicate that the homolytic bond dissociation energy (BDE) of the P–O bond in PO(OMe)$_2$ is higher than 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, 5' vs. 4' 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 phosphate radical cation is easier to cleave than that in the enol phosphate radical cation in agreement with our kinetic results.

The rate constants $k_1$ show that the enol phosphate radical cations 1' +, 2' + and 5' + [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$_2$=SiR$_3$], enol carbonate [MX$_2$=C(O)OR] and enol carbamate radical cations [MX$_2$=C(O)NR$_2$] because for these systems, $k_r$ is higher than 600 s$^{-1}$ in acetonitrile.\textsuperscript{10b,32} Equally, titanium enolate radical cation (Mes)$_2$C=C(H)OTiCP$_2$Cl$^+$ with $k_r=850$ s$^{-1}$ is more unstable than the enol phosphate radical cations.\textsuperscript{10b}

From the various compounds of the β,β-dimethylthiophenyl type studied hitherto, only trifluorocarboxyl radical cations have proved to fragment as slowly as the enol phosphate radical cations, e.g. (Mes)$_2$C=C(t-Bu)OC(O)CF$_3$ exhibiting $k_r=1.4$ s$^{-1}$.\textsuperscript{33}

In conclusion, we have prepared a series of phospho- enols and investigated their one-electron oxidation chemistry. Upon chemical or electrochemical oxidation, phospho- enol 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$_2$O$_5$. 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$_2$O$_5$ and filtered through basic alumina (ICN). Supporting electrolyte tetra- butyrammonium hexafluorophosphate (Fluka) was of electrochemical grade and used without further purification. Methyl(phenyl)phosphinic acid chloride\textsuperscript{14} and bis(diethylamino)chlorophosphine\textsuperscript{15} were prepared as described in the literature. Diethyl chlorophosphate, diphenyl chlorophosphate and diethyl chlorophosphate were purchased from Fluka and were used as received. \textsuperscript{1}$H$ 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 Bülchi 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 electron ionization (EI; 70 eV) conditions.

**(2,2-Dimethyl-1-phenylethenyl) diethyl phosphate (1).** A solution of 2,2-dimethyl-1-phenylethenyl (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): $\nu=2980$ cm$^{-1}$ (s, C–H), 2918 (s, C–H), 1611 (m, C=C–H), 1560 (w, aryl), 1477 (m), 1442 (m), 1276 (s), 1042 (s), 972 (s), 861 (m), 695 (m). $^1$H NMR (200 MHz, CD$_2$D$_6$, 298 K): $\delta=1.01$ (br s, 6 H, OCH$_2$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, OCH$_2$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), 7.69–7.95 (m, 3 H, Ph–H). $^1$H NMR (200 MHz, CD$_2$D$_6$, 333 K): $\delta=1.05$ (t, $J=7.1$ Hz, 6 H, OCH$_2$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, OCH$_2$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), 7.69–7.95 (m, 2 H, Ph–H). $^{13}$C NMR (50 MHz, CDCl$_3$): $\delta=15.83$ (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$_2$CH$_3$), 63.54 (d, $J_{P,C}=7.0$ Hz, 2 C, OCH$_2$CH$_3$), 127.10, 127.22, 127.61, 128.28, 128.92 (br s), 129.31, 134.46, 134.86, 134.92, 136.47, 136.56, 138.29, 139.01, 146.14 (C=C–O). $^{31}$P NMR (162 MHz, CDCl$_3$): $\delta=-5.67$ (s). MS-ES: [M/$m$/% rel. int.]: 492 (M$^+$, 16), 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$_{10}$H$_{17}$O$_4$P: C, 73.15%; H, 7.57%. Found: C, 72.84%; H, 7.25%.
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\(_3\)): \(\delta\) 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, \(J_{\text{p-c}}=7.5\) Hz, 2 C, OPh, C-1). \(^{31}\)P NMR (162 MHz, CDCl\(_3\)): \(\delta\) −5.15 (m, 9.94% (s). Analysis: calc. for C\(_{38}\)H\(_{60}\)O\(_3\)P: C, 77.53; H, 6.34%. Found: C, 77.48; H, 6.10%.}

(2,2-Dimethyl-1-phenylethyl) methyl phenyl phosphinate (3). A suspension of NaN\(_3\) (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): \(\tilde{\nu}\) 2936 cm\(^{-1}\) (m, C–H), 1609 (m, C=O), 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, \(\mathrm{C}_{6}\)D\(_6\)): 298 K): \(\delta\) 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. \(^{13}\)C NMR (50 MHz, CDCl\(_3\), TMS): \(\delta\) 16.59 (OCH\(_2\)CH\(_3\)), 16.68 (OCH\(_2\)CH\(_3\)), 20.78, 20.84, 21.05, 58.02 (OCH\(_2\)), 58.26 (OCH\(_3\)), 123.34 (C=C–O), 127.43, 127.92, 129.31, 135.68, 135.86, 136.16, 137.95, 139.08, 158.44 (C=C–O). \(^{31}\)P NMR (162 MHz, CDCl\(_3\), TMS): \(\delta\) 139.42 (s). Analysis: calc. for C\(_{38}\)H\(_{60}\)O\(_3\)P: C, 75.61; H, 7.83%. Found: C, 75.71; H, 8.06%.

(1,1-Dimethyl-3,3-dimethylbutyl-1-2-yl) diethyl phosphinate (5). A suspension of NaN\(_3\) (60 mg, 2.5 mmol) in anhydrous THF (4 ml) was treated with a solution of 1,1-dimethyl-3,3-dimethylbutyl-1-2-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, 5.2 g, 30 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, \(\mathrm{C}_{6}\)D\(_6\)): 298 K): \(\delta\) 1.01 (br s, 6 H, OCH\(_2\)CH\(_3\)), 1.36 (s, 9 H, C(CH\(_3\))\(_3\)), 2.02–2.25 (m, 3 H, Mes-CH\(_2\)), 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\(_2\)CH\(_3\)), 6.71–6.89 (m, 4 H, Mes-H); several signals are broadened because of coalescence. \(^{13}\)C NMR (50 MHz, \(\mathrm{C}_{6}\)D\(_6\)): \(\delta\) 15.92 (Mes-CH\(_3\)), 16.07 (Mes-CH\(_2\)), 20.62 (Mes-CH\(_3\)), 20.80 (Mes-CH\(_3\)), 21.83 (br, Mes-CH\(_3\)), 29.20 [5 C, OCH\(_2\)CH\(_3\) and C(CH\(_3\))\(_3\)], 39.66 [C(CH\(_3\))\(_3\)], 62.85 (d, \(J_{\text{p-c}}=4.5\) Hz, 2 C, OCH\(_2\)CH\(_3\)), 125.21, 125.33,
Diethylamino[bis(2,2-dimethyl-1-phenylenoxy)]- \lambda^3-
phosphane (6). A solution of 7 (1.0 g, 2.8 mmol) in
dichloromethane (10 ml) and acetonitrile (10 ml) was
pre pared first with triethylamine (0.52 ml, 3.8 g,
3.8 mmol) and then with bis(diethylamino)chloro-
phosphate35 (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 Al2O3; n-hexane-
dichloromethane 4:1, Rf 0.78) furnishing 390 mg
(0.48 mmol, 34%) of colorless crystals. M.p. 178–182°C
de (comp). IR (KBr): \(\bar{\nu} = 2919\) cm\(^{-1}\) (s, C–H), 1608 (m,
C=C), 1558 (m), 1444 (s), 1230 (m), 1193 (m), 1136 (m),
1019 (s, P–O–Ar), 903 (m), 849 (m), 744 (m), 691 (s).

\(^1\)H NMR (200 MHz, CDCl3, TMS): \(\delta 0.73\) (t, J =
7.3 Hz, 6 H, NCH2CH3), 1.91 (s, 6 H, Mes-CH3), 1.93
(s, 6 H, Mes-CH3), 1.95 (br s, 6 H, Mes-CH3), 2.14 (s,
6 H, Mes-CH3), 2.21 (s, 6 H, Mes-CH3), 2.23 (br s, 6 H,
6 H, -MesCH3), 2.32 (q, J = 7.3 Hz, 4 H, NCH2), 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, CDCl3, TMS): \(\delta 4.23\)
(NCH2CH3), 14.36 (NCH2CH3), 20.73, 20.78,
21.15, 21.33, 21.66, 22.03 (each one Mes-CH3), 37.43
(NCH2), 37.92 (NCH2), 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, CDCl3, TMS): \(\delta 143.12\)
(s). MS-ESI: m/z (% rel. int.) 814 (M + 1, 100), 741
(M – NEt3, 40), 355 (OPhC=CMes2, 30), 339
(Mes2C=CPH, 30). Analysis: calc. for C33H54O3P: C,
82.61; H, 7.93%; N 1.72%. Found: C, 81.98; H, 8.16;
N, 1.73%.

(1,1-Dimethyl-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 NaNH (63 mg,
2.6 mmol) in anhydrous THF (6 ml). The reaction mix-
ture was stirred for 1 h at room temp. and then treated
with diethyl chlorophosphate (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, Rf
0.56). A colorless oil was obtained which crystallized on
standing. Yield: 240 mg (0.60 mmol, 22%) of colorless
chemicals. M.p. 101–103°C. IR (KBr): \(\bar{\nu} = 3431\) cm
\(^{-1}\) (br s, O–H), 2962 (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). \(^1\)H NMR
(200 MHz, CDCl3, 298 K): \(\delta 0.34\) (t, J = 7.1 Hz, 3 H,
CH3), 0.65 [s, 9 H, C(CH3)3], 1.38–1.60 (m, 9 H,
Mes-CH3), 1.71–2.02 (m, 6 H, Mes-CH3), 2.36 (br s,
3 H, Mes-CH3), 3.14 (br s, 2 H, OCH2CH3), 6.08–6.27
(m, 4 H, Mes-H). \(^{31}\)P NMR (200 MHz, CDCl3, 333 K):
\(\delta 0.41\) (t, J = 7.9 Hz, 3 H, OCH2CH3), 0.65 [s, 9 H,
(C(CH3)3), 1.56 (s, 3 H, Mes-CH3), 1.57 (s, 3 H, Mes-
CH3), 1.64 (s, 3 H, Mes-CH3), 1.74 (s, 3 H, Mes-CH3),
1.90 (s, 3 H, Mes-CH3), 2.09 (s, 3 H, Mes-CH3),
3.06–3.21 (m, 2 H, OCH2), 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, CDCl3): \(\delta 16.17,
16.29, 20.69, 20.78, 21.11, 21.38, 22.11 (br s),
28.66 (OCH2CH3), 39.00 [C(CH3)3], 61.14 (d, J =
6.0 Hz, 1 C, OCH2), 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, CDCl3): \(\delta 2.81\) (s). MS-ESI:
m/z (% rel. int.) 428 (M*), 39, 303 (50), 263 (23), 262
(100), 261 (40), 247 (35), 246 (25). Analysis: calc. for C33H54O3P: 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 phospho-
enol were placed into two separate test tubes equipped with
stirring rods. On a high purity argon line, aceto-
nitrile (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 NaHCO3 (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 Na2SO4 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][PF6]2 which precipitates as a red solid. The
product mixture was analyzed by \(^1\)H NMR spectroscopy.
All products were identified by comparison with data of
authentic samples. Yields were determined by addi-
tion of m-nitroacetonitrile as an internal \(^1\)H 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 hexa-
fluorophosphate. 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 indi-
cated that conversion of the reactant was complete. The
brown solution was treated with dichloromethane

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(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 CaCl₂ 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, CDCl₃) δ 1.89 (s, 3 H, p-Mes-CH₃), 2.02 (s, 6 H, o-Mes-CH₂), 2.39 and 2.40 (two s, each 3 H, 4- and 6-CH₃), 2.54 (s, 3 H, 7-CH₃), 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).⁻⁰ ¹H NMR (250 MHz, CDCl₃) δ 1.20 [s, 9 H, C(CH₃)₃], 1.71 (s, 3 H, Mes-p-CH₃), 2.03 (s, 6 H, Mes-o-CH₂), 2.31 and 2.32 (two s, each 3 H, 4-CH₃ and 6-CH₃), 2.41 (s, 3 H, 7-CH₃), 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 acetoniitrile or dichloromethane (6 ml) was added by means of a gastight 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.²⁵ The working electrodes were self-made gold (diameter: 25 µm) and platinum (diameter: 10 µm) ultramicroelectrodes.

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References

16. All potentials are referenced to the ferrocene/ferrocinium (Fc) redox couple unless otherwise noted. To obtain values vs. SCE, simply add +0.39 V: (a) Röck, M., Ph.D. Thesis, University of Freiburg, Freiburg 1994; this conversion is in excellent agreement with literature values: (b) Connelly, N. G. and Geiger, W. E. Chem. Rev. 96 (1996) 877.
17. Peak potentials E_{p1} are given for irreversible peaks, whereas for reversible waves the halfwave potentials E_{1/2} are presented.
20. Pandey, G., Pooranchand, D. and Bhalerao, U. T. Tetrahedron 47 (1991) 1745. The redox potential is provided against the saturated calomel electrode: E_{1/2} = 1.57 V_{SCE}.

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