Enol Cation Radicals in Solution, 3[1]

Reaction of Enol Cation Radicals in the Presence of Nucleophiles

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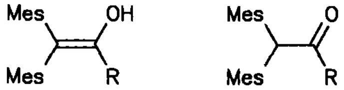
The one-electron oxidation chemistry of three diaryl-substituted enols, 1,1-dimesityl-1-propen-2-ol (**7**), 1,2-dimesityl-1-propen-1-ol (**8**), and 2-mesityl-2-phenylethenol (**9**), has been examined. As a consequence of the pronounced steric shielding around the β-carbon, **7** does not react with nucleophiles upon addition of 2 eq. of oxidant, but cyclizes to yield benzofuran **18**. Under identical conditions, the less shielded enols **8** and **9** react with methanol and other nucleophiles. Several mechanistic hypotheses for nucleophile incorporation are tested, thus allowing the second part of the α-umpolung reaction of ketones via enol cation radicals to be elucidated mechanistically. Fast-scan cyclic voltammetry studies (2000 V $\cdot$ s^{-1}) show no reversible wave of the enol cation radicals. The corresponding methyl enol ether cation radicals, however, have a lifetime of several seconds at -10°C, and the kinetics of their reactions with acetonitrile and methanol was probed. The results obtained are consistent with fast deprotonation being the primary reaction of enol cation radicals. Under the given oxidative conditions the radicals formed are further oxidized. Consequently one-electron oxidation of enols provides an interesting entry to α-carbonyl carbocation chemistry.

Our incentive to study the one-electron oxidation chemistry of enols stems from the fact that enol cation radicals are much more stable than the corresponding tautomeric ketone ions, in distinct contrast to the thermochemistry of the neutral species[2]. Only very recently[3] it has been shown that this inversion of thermochemistry upon one-electron oxidation applies to the solution phase as well. As a consequence, enols are much easier to oxidize than the tautomeric ketones, often by a potential difference of close to one volt.



1 (R : tBu) 3
2 (R : H) 4
Mes: $2,4,6-(H_3C)_3C_6H_2$

Table 1. Peak potentials E_p (vs. SCE) of enols and ketones **1**–**4** and reaction free energies[a] in acetonitrile

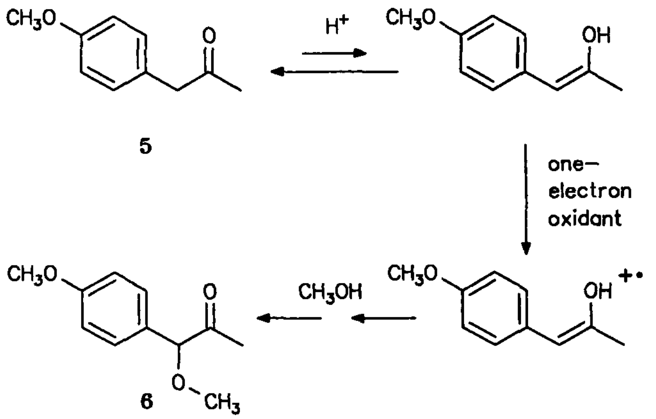
E_p(enol) [V]	E_p(ketone) [V]	$\Delta G°$(enol→ketone) [kcal·mol^{-1}]	$\Delta G°$(enol$^{+\bullet}$→ketone$^{+\bullet}$) [kcal·mol^{-1}]
1: 0.97	**3**: 1.85	-2.6	17.7
2: 1.00	**4**: 1.98	+3.1	25.7

[a] Ref.[3].

This opens up a very straightforward approach to enol cation radical chemistry starting from the parent ketone as a stable precursor. When selecting a proper one-electron oxidant it ought to be possible to selectively oxidize the enol present at a small concentration besides the ketone in the equilibrium. If enolization (acid- or base-catalyzed) is faster than endergonic electron transfer from the ketone to the one-electron oxidant then the ketone can quantitatively be transformed to the enol cation radical.

With model systems like (4-methoxyphenyl)acetone (**5**) this approach has successfully been applied to design an α-umpolung reaction[4] for ketones via enol cation radicals.

Scheme 1



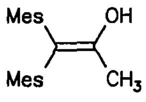
While all the experimental data point to enol cation radicals as reactive intermediates in the above reaction it is still unclear how they react to ultimately afford α-substituted ketones (e.g. **6**). Therefore, we decided to have a closer look at the reactions of enol cation radicals with nucleophiles to test a) their intrinsic chemistry and b) the validity of the hypothesis forwarded above.

Hitherto, the study of enol cation radicals in solution[5] has been largely neglected mostly due to the instability of enols in solution. The intense work in enol chemistry[6,7] during the past decade, however, has made new routes to enols accessible in solution.

In order to directly study the one-electron oxidation chemistry of enols, we have turned to a series of so-called "simple enols"[8], that had originally been discovered by Fuson[9] and later studied in detail by Rappoport[7].

Model Compounds

We have synthesized three stable enols **7**, **8**, and **9** according to procedures given by Fuson[9] and Rappoport[10]. All compounds can be obtained in a tautomerically pure form because they are not only thermodynamically but also kinetically stabilized by the mesityl groups. Enols **8** and **9** have been chosen because steric congestion around the β-carbon is much less pronounced than in **7**, thus allowing bimolecular reactions of the enol cation radicals with nucleophiles.



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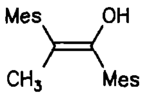

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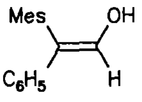

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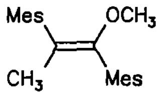

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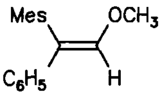

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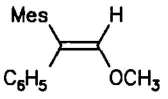

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While enols **7** and **8** have been characterized in detail by Rappoport[10], the structure of **9** has only tentatively been assigned by Fuson[9]. Therefore, we have determined the structure of **9** by ^{1}H-NMR difference NOE experiments and assigned a *Z* configuration, in agreement with unpublished X-ray data by Rappoport[11].

For comparison we include some control experiments on the one-electron oxidation of enols **1** and **2** which have partly been reported earlier[3].

Whereas enol ether **10** has been described by Fuson[12] in detail, he obtained $MesPhC{=}C(OCH_3)H$[9b] only as a mixture of isomers. After using his procedure to synthesize the enol ether mixture we have been able to separate the two stereoisomeric enol ethers **11** and **12** by chromatography[13].

Cyclic Voltammetry

To probe the stability and reactivity of the cation radicals $7^{+\cdot}$, $8^{+\cdot}$, and $9^{+\cdot}$ we have recorded the cyclic voltammograms (CV) of the parent enols in acetonitrile. All cyclic voltammograms show an irreversible oxidation wave (up to $0.5\ V \cdot s^{-1}$), thus pointing to fast subsequent reactions of the enol cation radicals in agreement with earlier observations[3] made for enols **1** and **2**. The observed low peak potentials of **7**–**9** are in line with the known low ionization potentials of enols[14].

Unlike CV studies on similar enols **1** and **2**[3] the enol oxidation waves were not followed by a pronounced second, anodically shifted wave that would indicate fast benzofuran formation on the CV time scale.

In addition, all the enols were studied at room temperature in acetonitrile at high scan rates (up to $2000\ V \cdot s^{-1}$) by using ultramicroelectrode CV[15]. Only irreversible waves were observed upon oxidation, thus providing a rough estimate for the lower limit of the subsequent reaction ($k > 6 \cdot 10^4\ s^{-1}$) of the enol cation radicals. The fast-scan CV studies were undertaken in the laboratory of Amatore (Paris) and the experimental setup has been described earlier[16].

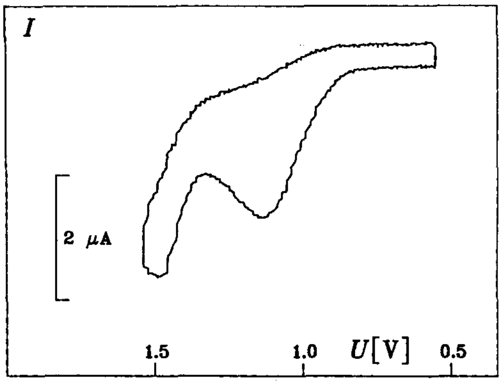


Figure 1. CV curve of **2** in acetonitrile at a 10 μm Pt disc ultramicroelectrode ($v = 2000\ V \cdot s^{-1}$)

In contrast to the irreversible enol waves the cyclic voltammograms of enol ethers **10**, **11**, and **12** show quasi-reversible waves at low temperatures under suitable conditions.

Table 2. Oxidation potentials of enols and enol ethers (vs. SCE) at $0.1\ V \cdot s^{-1}$ in acetonitrile or dichloromethane

Enol	E_{ox} [V]	Remarks
7	1.01	peak pot.[a], irrev.[b], CH_3CN
8	1.26	peak pot.[a], irrev.[b], CH_3CN
9	1.08	peak pot.[a], irrev.[b], CH_3CN
10	1.32	$E_{1/2}$, quasi-rev.[c], CH_3CN, -10°C
11	1.23	$E_{1/2}$, quasi-rev.[c], CH_2Cl_2, -10°C
12	1.20	$E_{1/2}$, quasi-rev.[c], CH_2Cl_2, -10°C

[a] Peak potential. — [b] Irreversible wave. — [c] Quasi-reversible wave.

Since fast-scan CV studies did not allow the subsequent reactions of enol cation radicals to be monitored, we have used the high stability of the enol ether cation radicals to probe the kinetics of their reaction with nucleophiles by CV. Applying the kinetic scheme derived by Shain and Nicholson[17] for the analysis of cyclic voltammograms, we were able to extract the pseudo-first-order rate constant for the reaction of $10^{+\cdot}$ and $11^{+\cdot}$ with the solvents acetonitrile and dichloromethane. For the determination of second-order rate constants, i.e. the reaction of $10^{+\cdot}$ with methanol and $11^{+\cdot}$ with either methanol or acetonitrile, the analysis developed by Savéant was used[18]. In this approach the reaction was assumed to be first order with respect to cation radical and nucleophile[18,19], thus providing an upper limit for the second-order rate constants.

Table 3. Rate constants[a] for the reaction of enol ether cation radicals with acetonitrile and methanol at 266 K

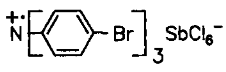
Enol ether	k (solvent) [s^{-1}]	k (nucleophile)[b] [$M^{-1} \cdot s^{-1}$]
10	0.1 (AN)	$< 3 \cdot 10^2$ (MeOH)[c,d]
10	0.03 (CH_2Cl_2)	
11	0.5 (CH_2Cl_2)[e]	$< 7 \cdot 10^2$ (MeOH)[c,f]
11	0.7 (CH_2Cl_2)[g]	< 7 (AN)[f,h]

[a] Measured in given solvent with 0.1 M *n*-butylammonium hexafluorophosphate as electrolyte, AN: acetonitrile. — [b] Analysis according to refs.[18,19]. — [c] $c_{MeOH}/c_{enol\ ether} = 2:1$. — [d] In acetonitrile. — [e] According to the kinetic analysis from ref.[17]. — [f] In dichloromethane. — [g] According to the kinetic analysis from ref.[18]. — [h] $c_{AN}/c_{enol\ ether} = 100:1$.

The rate constants reported in Table 3 are preliminary data[19] of a detailed kinetic study on the reactions of stable enol ether cation radicals the complete results of which will be reported in due course.

Reactions

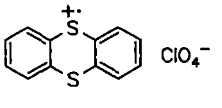
We have chosen three different one-electron oxidants, tris(*p*-bromophenyl)aminium hexachloroantimonate (**13**)[20], tris(*o*-phenanthroline)iron(III) hexafluorophosphate (**14**)[21], and thianthrenium perchlorate (**15**)[22] to perform the oxidation reactions in either pure acetonitrile or acetonitrile/nucleophile-solvent mixtures at room temperature. The product yields obtained proved to be almost independent of the used oxidant. As **14** has been shown by Kochi[23] to behave as an outer-sphere one-electron oxidant in reactions with aromatic compounds we assume all the oxidation reactions to start by the primary formation of an enol cation radical.



13
(1.06 V)

$Fe(phen)_3(PF_6)_3$

14
(1.09 V)



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(1.28 V)

The reaction of **7** or **8** with 200 mol-% of a one-electron oxidant in acetonitrile as weakly nucleophilic solvent resulted in predominant formation of benzofurans **18** and **19**. No products of solvent incorporation could be found. This reaction mode has been observed earlier for the oxidation of the similar enols **1** and **2**[3].

Oxidation of the enols **1** and **2**, after addition of 100 mol-% of tetramethylammonium hydroxide to generate the enolates, with 200 mol-% of oxidant **14** also afforded the benzofurans **16** (72%) and **17** (52%).

Scheme 2

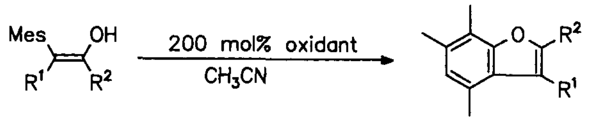

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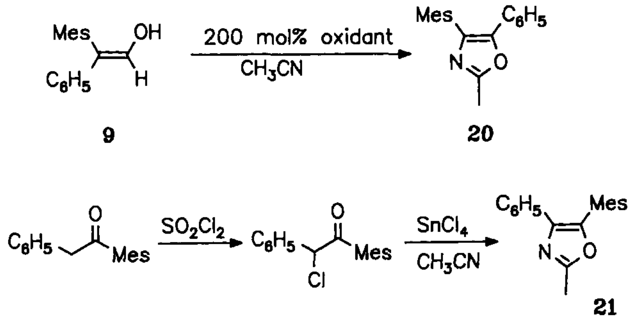
Table 4. Yields of the enol oxidation reaction by using 200 mol-% of various one-electron oxidants

Oxidant	Enol	R^1	R^2	Products
13	**1**	Mes	tBu	**16** (82%)[a]
14	**1**	Mes	tBu	**16** (91%)[a]
13	**2**	Mes	H	**17** (85%)[a]
14	**2**	Mes	H	**17** (81%)[a]
13	**7**	Mes	CH_3	**18** (84%)
14	**7**	Mes	CH_3	**18** (75%)
13	**8**	CH_3	Mes	**19** (70%), **24** (23%)
14	**8**	CH_3	Mes	**19** (58%)
15	**8**	CH_3	Mes	**19** (87%)

[a] Ref.[3].

In contrast to the reactions of **7** and **8**, the oxidation of **9** with 200 mol-% of **13** or **14** in acetonitrile furnished oxazole **20** as the sole product in 85 and 68% yield, respectively. We have determined the structure of **20** by an independent synthesis of its isomer **21** according to a procedure described by Lora-Tamayo[24]. Attempts to synthesize **20** by means of the same strategy failed because of problems arising in the synthesis of the corresponding 2-chloro-2-mesityl-1-phenylethanone. The positional isomer **21** could not be detected by ^1H- or ^{13}C-NMR spectrometry in the one-electron oxidation of **9**.

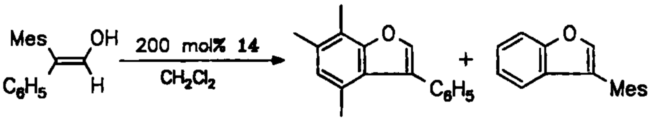
Scheme 3



Obviously **20** is generated by nucleophilic attack of acetonitrile on $9^{+\cdot}$ or a subsequently formed cationic intermediate. In contrast, when steric shielding around the β-carbon of the enol is increased as in **2** only intramolecular cyclization to the corresponding benzofuran is observed after oxidation (see Table 4).

To probe whether intramolecular cyclization of enol **9** to the corresponding benzofuran would take place in the absence of a nucleophile the oxidation reaction was performed in dichloromethane. Using **14** as oxidant, we obtained two isomeric benzofurans **22** and **23**, that could not be separated but were identified by their spectral data. **9** recovered after partial *conversion has* proved to be isomerically pure *Z*-**9**. Thus, we believe that the loss of stereochemistry must occur after the initial oxidation step.

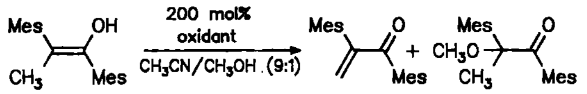
Scheme 4



9 **22** (12%) **23** (26%)

Although the enols used in this study exhibit similar structural features the reactions of the corresponding cation radicals in the presence of added methanol or water proceeded quite distinctly. Thus, the oxidation of **7** in acetonitrile/methanol (9:1) or in acetonitrile/water (9:1) resulted again in the exclusive formation of benzofuran **18**, albeit in much lower yield (40%). No product of nucleophile incorporation could be detected. In contrast, **8** was converted into a mixture of two new products when oxidized in acetonitrile/methanol (9:1).

Scheme 5



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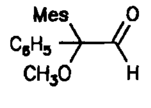
	24	**25**
13	56%	23%
14	54%	27%

The main product could be identified as **24**, the direct precursor of **8** in the synthesis according to Fuson[9a]. The minor product **25** showed incorporation of methanol. **24** does not arise from acid-catalyzed methanol elimination from **25** since addition of 2,6-di-*tert*-butylpyridine to the reaction mixture did not change the relative yields. Intramolecular cyclization to **19** does not take place. Oxidation in acetonitrile/water (9:1) afforded **24** in 58% (with **13**) and 73% yield (with **14**), respectively. Hydroxylation occurred to less than 5% as evidenced by a GC-MS analysis.



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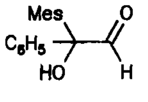

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Finally the reaction of enol **9** under the conditions described for the oxidation of enol **8** resulted in predominant formation of α-methoxy- and α-hydroxy aldehydes **26** and **27**.

Tab. 5. Products of the one-electron oxidation of **9** in acetonitrile/methanol (9:1) or acetonitrile/water (9:1)

Oxidant	Nucleophile	Products[a]				
		26	**27**	**11**	**20**	**23**
13	methanol	57%	–	17%	16%	–
14	methanol	41%	–	35%	–	–
13	water	–	38%	–	–	25%
14	water	–	57%	–	18%	25%

[a] Yields determined by ^{1}H-NMR spectrometry using an internal standard.

Discussion

The formation of **20**, **25**, **26**, and **27** in the presence of nucleophiles supports the proposed mechanism for the α-umpolung of ketones via intermediate enol cation radicals. The possibility to either start from stable simple enols or ketones and to observe the same one-electron oxidation chemistry allows for the first time the details of the α-umpolung of ketones to be elucidated mechanistically.

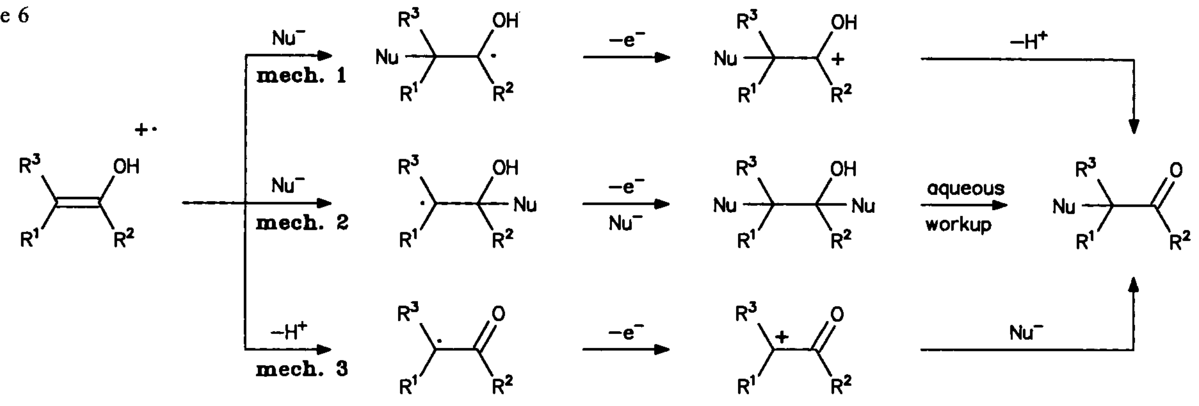
To explain the formation of **20**, **25**, **26**, and **27** three mechanistic hypotheses can be forwarded, the first two differing only in the regiochemistry of the attack of the nucleophile on the enol cation radical. The third mechanism invokes deprotonation of the enol cation radical, followed by a second oxidation step and reaction of the α-carbonyl *carbo*cation with nucleophiles.

The formation of benzofurans **16**–**19** and **22**, **23** can be explained analogously. The enol cation radical can either cyclize directly (intramolecular nucleophilic attack; mechanism 4) or deprotonate (mechanism 5). The deprotonation mechanism was suggested by Bailey in 1970[25] to explain the formation of 2–3% 2,3-dimesityl-4,6,7-trimethylbenzofuran upon ozonation of trimesitylethenol. Further studies by Bailey[26], however, did not support the involvement of enol cation radical intermediates, and a mechanism based on hydrogen abstraction from trimesityl-ethenol by ozone was postulated.

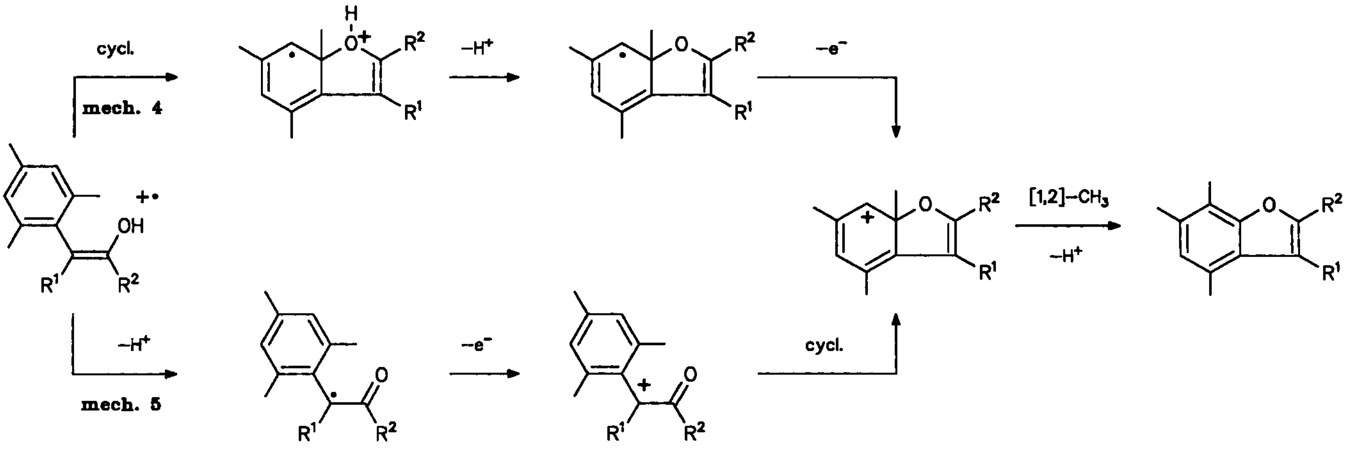
In principle, the mechanistic differentiation between the various mechanisms is straightforward. A simple OH/OD isotope effect study on the lifetime of the enol cation radicals should provide the answer. However, all our attempts to detect enol cation radicals as short-lived intermediates have been unsuccessful so far. Neither ultramicroelectrode cyclic voltammetry (up to 2000 V · s^{-1}) nor preliminary flash photoionization studies have exhibited any sign of the cation radicals. As a consequence, the subsequent reactions of the enol cation radicals have to be of the order of at least $k > 6 \cdot 10^4$ s^{-1}.

Although the high reactivity of enol cation radicals has precluded the OH/OD isotope study so far, the results ob-

Scheme 6



Scheme 7



tained in this study provide convincing evidence to differentiate between the mechanistic hypotheses. According to our CV results, replacing OH in **8** or **9** by OCH_3 greatly increased the stability of the corresponding cation radicals. Obviously, the increased stability of the enol ether cation radicals can be traced down to the lack of the OH functionality, proposing that deprotonation (mech. 3) is the main route for enol cation radicals. To further corroborate this suggestion we have measured the rates of the reaction of two nucleophiles with enol ether cation radicals by CV. The rate constants obtained for the reaction of $\mathbf{10}^{+\cdot}$ and $\mathbf{11}^{+\cdot}$ with methanol proved to be extremely low, i.e. $k = 3 \cdot 10^2$ and $k < 7 \cdot 10^2\ M^{-1} \cdot s^{-1}$ (at $-10\,°C$). Even much slower was the reaction of $\mathbf{11}^{+\cdot}$ with acetonitrile ($k < 7\ M^{-1} \cdot s^{-1}$ at $-10\,°C$). If we agree on the assumption that the rate constant for nucleophilic attack on the enol cation radicals $\mathbf{8}^{+\cdot}$ and $\mathbf{9}^{+\cdot}$ will not differ essentially from the one measured with the enol ether cation radicals $\mathbf{10}^{+\cdot}$ and $\mathbf{11}^{+\cdot}$, then the measured rates for nucleophilic attack are much too low to explain the short lifetime of the enol cation radicals. Therefore, all experimental evidence is convincingly arguing against direct nucleophilic attack (mech. 1 or 2) on the enol cation radicals. Apparently, deprotonation will occur at least some orders of magnitude faster.

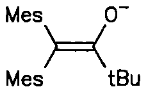
Various literature reports advocate the idea that nucleophilic attack on olefin cation radicals is a slow reaction[27] compared to carbocation-nucleophile reactions. The valence bond configuration mixing model as developed by Shaik and Pross[28] has successfully been used to explain the low reactivity of cation radicals toward nucleophiles. Interestingly, this straightforward simple semiquantitative picture can also rationalize the very few exceptions, where nucleophilic attack is extraordinarily fast, e.g. in the case of ketene$^{+\cdot}$ and ammonia[29]. Nevertheless, the model has been criticized for its failure to explain the low barrier for the 9-phenylanthracene cation radical/pyridine reaction[30] and, even after a revision of the theory by Parker[31], the usefulness of the predictions is still not perfectly clear[32]. In the light of the ongoing controversy it was interesting to compare the predictions with our rate constants.

Applying Shaik's and Pross' model, we can estimate the relevant energy gaps G for the reaction of $\mathbf{9}^{+\cdot}$ with the nucleophiles by $G = IP_s(\text{Nu}) - EA_s(\mathbf{9}^{+\cdot}) + E_{ST}(\mathbf{9})$[28]. By using the appropriate solution ionization potentials $IP_s(\text{MeOH}) = 223.4$ kcal/mol and $IP_s(\text{MeCN}) = 255.8$ kcal/mol[33], a solution electron affinity $EA_s(\mathbf{9}^{+\cdot}) = 142.7$ kcal/mol[34] and a singlet-triplet excitation energy $E_{ST}(\mathbf{9}) = 59$ kcal/mol[35], we have obtained an energy gap G of 139.7 kcal/mol and 172.1 kcal/mol for $\mathbf{9}^{+\cdot}$/MeCN, respectively.

As a rule of thumb reactions whose initial energy gap G is 60 kcal/mol or less will be rapid, while such with $G > 100$ kcal/mol will be slow[28]. Therefore, according to the configuration mixing theory, both the reaction of $\mathbf{9}^{+\cdot}$ with acetonitrile and with methanol are expected to be sluggish in agreement with the predictions made on the basis of our experimental rates for the enol ether cation radicals.

The mechanistic proposal, that deprotonation of the enol cation radicals proceeds faster than reaction with nucleophiles, is also in line with their high acidity. We have determined the acid dissociation constants of the enol cation radicals in acetonitrile by using a thermochemical cycle proposed by Arnold[36] and have obtained the following pK_a values: 6.2 ($\mathbf{1}^{+\cdot}$), 5.7 ($\mathbf{2}^{+\cdot}$), 5.6 ($\mathbf{7}^{+\cdot}$), 4.4 ($\mathbf{9}^{+\cdot}$) and 1.3 ($\mathbf{8}^{+\cdot}$)[37]. This corresponds to a pK_a value of 2.60 for trifluoromethanesulfonic acid in acetonitrile[38]. According to the pK_a values deprotonation of $\mathbf{1}^{+\cdot}$ should be pushed back by the addition of CF_3SO_3H. However, even in the presence of a 3-fold excess of CF_3SO_3H vs. **1** the CV still exhibited an irreversible oxidation wave (at 0.5 V · s^{-1}). Obviously, a fast subsequent reaction, i.e. oxidation of the resulting α-carbonyl radical (see mechanism 3), determines the fate of the enol cation radical. A prerequisite for a fast oxidation of the intermediate radical is that its oxidation potential is lower than that of the parent enol. This is confirmed by AM1 calculations showing that the IP_a of **9** is ca. 0.6 V higher than that of MesPhC$^\cdot$ – CHO[39].

The validity of mechanisms 3 and 5 can further be substantiated by our studies on enolate oxidation. Oxidation of enolates **28** and **29** in the presence of 200 mol-% of one-electron oxidants provided the benzofurans **16** and **17** in good yields, supporting the involvement of α-carbonyl radicals **30** as reactive intermediates in both enol and enolate oxidation.



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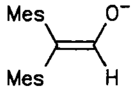

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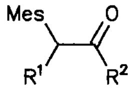

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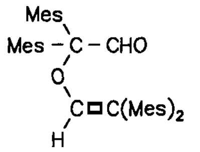


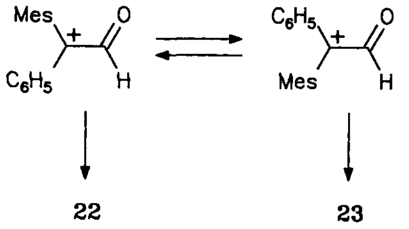
31

The evidence collected so far clearly suggests that the enol cation radicals undergo very rapid proton loss like the analogous phenol cation radicals[40]. The same conclusion can be drawn from studies by Schäfer[41] and Yoshida[5a] on the anodic oxidation of enols of β-dicarbonyl compounds, since radical-derived products were found. However, in contrast to the β-dicarbonyl systems α-carbonyl radicals with aryl substituents are easier to oxidize than the parent enols[39]. Therefore, α-carbonyl carbocations are formed rapidly in our systems either by disproportionation or oxidation by an added oxidant. As a consequence, the observed chemistry is derived from intermediate carbocations which can either cyclize to benzofurans or react with external nucleophiles. Benzofuran formation from aryl-substituted α-carbonyl cations has been demonstrated by Okamoto's elegant study on the chemistry of the isolated p-(4-methoxybenzoyl)bis(4-methoxyphenyl)methylium hexafluoroantimonate[42].

Fast oxidation of α-carbonyl radicals to α-carbonyl cations under our reaction conditions is further corroborated by the lack of radical-derived products, i.e. dimerization products. Although the model enols are sterically encumbered, dimerization of the corresponding α-carbonyl radicals is still feasible as demostrated by Bailey's ozonation studies[25]. In these investigations it was shown that radical **30** (R^1 = Mes, R^2 = H) dimerized to **31** (53%), a product already obtained upon hypochlorite oxidation of **2** by Fuson[43].

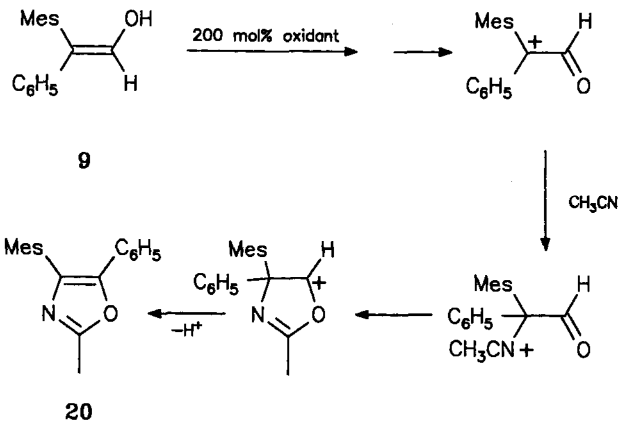
Thus, the formation of the two isomeric benzofurans **22** and **23** could readily be explained by rotation around the former CC-double bond at the stage of the α-carbonyl carbocation intermediate[44]. According to calculations by Houk and others[45] the rotational barrier of a CHO group in a α-carbonyl carbocation may be as low as 2.5 kcal/mol.

Scheme 8



The formation of oxazole **20** in the oxidation reaction of enol **9** is reminiscent of the various oxidation studies of heteroallyl systems by Shine[46]. The intermediate nitrilium adduct can cyclize and after a Wagner-Meerwein rearrangement oxazole **20** is formed. The predominant formation of **20** over **21** can be rationalized by a much faster 1,2-shift of the phenyl residue as compared to the mesityl group.

Scheme 9



When comparing the various enol oxidation reactions in the presence of nucleophiles it becomes obvious that only the least sterically hindered enols **8** and **9** undergo intermolecular reactions to incorporate external nucleophiles. Not even **2**, the least sterically hindered enol of the β,βdimesityl enols, is prone to a reaction with methanol under oxidative conditions. Obviously, the shielding of the β-carbon prohibits attack of any external nucleophile on the α-carbonyl cation therefore leading exclusively to intramolecular cyclization.

At this point it is illustrative to compare the solution- and the gas-phase chemistry of enol cation radicals, as exemplified by $\mathbf{2}^{+\cdot}$. While the solution-phase chemistry is dominated by deprotonation as a result of the high solvation energy of the proton and subsequent oxidation, the ion in the gas phase exhibits a variety of specific rearrangements that could only recently be identified. Several processes, decomposition of $\mathbf{2}^{+\cdot}$ via intermediate $\mathbf{4}^{+\cdot}$, hydrogen transfer from one *ortho*-methyl group to the α-carbon of the enol, and a reciprocal methyl/hydrogen transfer are competing with each other[14,47]. Hence, it is the limitation of enol cation radicals in solution to one dominant reaction channel that allows the control of their chemistry.

To sum up, the dominant reaction of enol cation radicals in solution involves fast proton loss. The formed intermediate α-carbonyl radicals are easily oxidized (either by an external oxidant or by disproportionation) to α-carbonyl cations that can either cyclize, deprotonate or react with nucleophiles. In addition, these studies on stable simple enols have substantiated the occurrence of intermediate enol cation radicals in the α-umpolung of ketones[4].

We gratefully acknowledge financial support from the *Wissenschaftliche Gesellschaft Freiburg* and the *Volkswagenstiftung* and thank the *BASF* for a scholarschip for M.R. We are indebted to *D. Morat* for laboratory assistance, to Dr. *C. Amatore* (Paris) for his help with ultramicroelectrode CV studies, to Dr. *S. Steenken* (Mülheim) for some preliminary photoionization experiments on various enols and to Prof. *C. Rüchardt* for generous support of our work.

Experimental

^{1}H NMR: 90 MHz, Varian EM 390; 250 MHz, Bruker WM 250; 400 MHz, Bruker AM 400; internal standard: TMS. – ^{13}C NMR: 20 MHz, Bruker WP 80; 100 MHz, Bruker AM 400; internal standard: TMS. – IR: Perkin-Elmer 421 and 398. – MS: Finnigan MAT 44 S. – UV: Zeiss DMR 21 and PMQ 3. – Microanalyses: Perkin-Elmer Elemental Analyzer 240. – Melting points were not corrected. – Cyclic voltammetry: The CV measurements were performed in a electrochemical cell by using a platinum disk (1.0 mm diameter) working electrode, a platinum auxiliary electrode and a Ag/AgCl reference electrode. All potentials were referenced to internal ferrocene[15]. The potential measurements were made on a 1 mM solution of the substrate in acetonitrile with tetra-*n*-butylammonium hexafluorophosphate (0.1 M) as the supporting electrolyte at a scan rate of 0.1 V · s^{-1}. – GC: Carlo Erba fractovap 4130, GC 6000 (Vega Series) and GC 5130 (Mega Series) using capillary columns. – Glovebox: MBraun 120B. – When possible the products were isolated, fully characterized and their purity determined by GLC. In cases, where isolation was not possible, the structure was assigned on the basis of ^{1}H-NMR, IR and GC/MS data. Compound **24** has been described earlier[9a].

Purification of Solvents and Reagents: Commercial *acetonitrile* was refluxed from phosphorus pentoxide, potassium permanganate/lithium carbonate, potassium hydrogen sulfate, and from calcium hydride[48]. The last distillation was performed under purified argon. Acetonitrile was stored under argon. Dichloromethane: Distilled from phosphorus pentoxide and chromatographed over basic alumina, stored under argon. – *Tris(p-bromophenyl)aminium hexachloroantimonate* (**13**): The commercial product (Janssen; Aldrich) was thoroughly washed with anhydrous diethyl ether and stored in the glove box. – *Tris(o-phenanthroline)iron(III) hexafluorophosphate* (**14**): Prepared according to the procedure described in ref.[22]; photometrical determination of the iron(III) content. – *Thianthrenium perchlorate* (**15**): Prepared according to a known procedure[49]. – *Silica gel:* MN 60 from Macherey & Nagel.

Syntheses of Enols: 1,1-Dimesityl-3,3-dimethyl-1-buten-2-ol (**1**), *2,2-dimesitylethenol* (**2**), *1,1-dimesityl-1-propen-2-ol* (**7**), *1,2-dimesityl-1-propen-1-ol* (**8**), *2-mesityl-2-phenylethenol* (**9**) were prepared according to known procedures[9,10].

Syntheses of Enol Ethers: A mixture of *(Z)-1-mesityl-2-methoxy-1-phenylethene* (**11**) and *(E)-1-mesityl-2-methoxy-1-phenylethene* (**12**) was obtained by using the procedure described by Fuson[9b]. The two isomers could be separated by chromatography on silica gel using hexane/ethyl acetate (10:1) as eluent[13].

(Z)-1,2-Dimesityl-1-methoxy-1-propene (**10**): A solution of 1.00 g (3.40 mmol) of **8** and 2.20 g (23.4 mmol) of dimethyl sulfate in 7 ml of anhydrous methanol was refluxed under N_2. A solution of 2.00 g (35.0 mmol) of KOH in 10 ml of anhydrous methanol was slowly added while stirring. After the addition had been completed refluxing was continued for 30 min. The reaction mixture was poured into 50 ml of water, the precipitate was filtered off, and the solid dried in vacuo to provide 0.53 g (52%) of crude material. Recrystallization from anhydrous ether (–10°C) afforded 0.22 g (21%) of pure material (>98%), m.p. 170–172°C (ref.[12] 170–179°C). – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1}, 2850 (OCH_3), 1650 (C=C), 1600 (C=C). – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.51 (s, 3H), 2.26 (s, 3H), 2.30 (s, 3H), 2.32 (s, 6H), 2.37 (s, 6H), 3.09 (s, 3H), 6.88 (s, 2H), 6.92 (s, 2H). – ^{13}C NMR (100 MHz, $CDCl_3$): δ = 17.74, 20.53, 20.63, 21.08, 21.17, 54.83, 113.25, 128.38 (C-3′, C-3″), 130.82, 135.70, 135.78, 137.57, 137.79, 137.98, 147.87. – MS (EI, 70 eV): *m/z* (%) = 308 (80) [M^+], 261 (100), 246 (40), 157 (20), 147 (10), 119 (10). – MS (CI, NH_3): *m/z* (%) = 326 (100) [$M + NH_4^+$].

$C_{22}H_{28}O$ (308.5)	Calcd.	C 85.66	H 9.15
	Found	C 85.16	H 9.18

General Procedure for the One-Electron Oxidations of the Enols: In a glove box 100 μmol (200 mol-%) of the one-electron oxidant was placed into a test tube equipped with a stirring rod. The tube was capped with a septum stopper, removed from the glove box and hooked up to a high-purity argon line. 1.0 ml of purified acetonitrile was added through a syringe to dissolve the oxidant. In a second test tube with a septum cap a solution of 50 μmol (100 mol-%) of the enol in 1.0 ml of acetonitrile (alternatively 0.8 ml of acetonitrile and 0.2 ml of nucleophile) was prepared under argon and transferred through a syringe to the oxidant solution. This solution decolorized immediately upon addition of the enol solution. To quench the reaction 1.5 ml of sat. aqueous $NaHCO_3$ was added, and the reaction mixture was diluted by the addition of dichloromethane (10 ml). The products were extracted with dichloromethane (3 times) and the combined organic layers washed once with brine. After drying the organic layers with Na_2SO_4, the solvent was removed by rotary evaporation yielding the crude product. In the reactions using **14** as oxidant the iron salts were separated by extracting the organic product into diethyl ether and filtering off undissolved Fe(II)-phenanthroline salts. Product analysis was performed by using GC/GC-MS and ^{1}H NMR. To obtain quantitative data a known amount of *m*-nitroacetophenone was added as a standard to the NMR solution. To identify the oxidation products the crude product mixtures were separated by chromatography and the single components identified by their spectral data or by a comparison with compounds synthesized independently.

General Procedure for the One-Electron Oxidation of Enolates: According to the general procedure above the enolates **28** and **29** were prepared in situ by the addition of 1 eq. of tetramethylammonium hydroxide prior to their reaction with the one-electron oxidant.

Benzofurans **16**–**19** were synthesized by using the general procedure for enol oxidation in pure acetonitrile. Alternatively, oxidation of enolates **28** and **29** provided the benzofurans (**16**: 72%; **17**: 52%), too. The spectral data of **16** and **17** have been reported earlier[3].

3-Mesityl-2,4,6,7-tetramethylbenzofuran (**18**) was synthesized in 75% yield from 13 mg (44 μmol) of enol **7** by oxidation with 2 eq. of **14** according to the general procedure. Purification by chromatography using cyclohexane/dichloromethane (2:1, R_f = 0.73) afforded pure **18** (purity >98.3%): IR (NaCl): $\tilde{\nu}$ = 3000 cm^{-1} (CH), 2900, 1635 (C=C), 1600 (C=C), 1450, 1370, 1300, 1210, 1100, 930, 910, 850, 730. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.85 (s, 3H), 2.00 (s, 6H), 2.18 (s, 3H), 2.33 (s, 6H), 2.42 (s, 3H), 6.70 (s, 1H), 6.93 (s, 2H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 11.47, 12.12, 17.12, 19.05, 20.52, 21.24, 27.01, 116.75, 124.94, 125.40, 127.47, 127.85, 130.08, 131.30, 137.01, 138.05, 149.58, 153.85. – MS (EI, 70 eV): *m/z* (%) = 292 (100), 277 (37), 262 (12), 234 (16), 157 (24), 146 (20), 131 (22). – MS (CI; NH$_3$): *m/z* (%) = 293 (100) [M + H$^+$].

$C_{21}H_{24}O$ Calcd. 292.1827 Found 292.1825

2-Mesityl-3,4,6,7-tetramethylbenzofuran (**19**): According to the general procedure 50 mg (170 μmol) of enol **8** was oxidized with 2 eq. of **14** to afford 92% of **19**. The benzofuran was purified by chromatography using cyclohexane as eluent (R_f = 0.44): IR (CCl$_4$): $\tilde{\nu}$ = 3000 cm^{-1}, 2900, 1700, 1610, 1600, 1440, 1380, 1320, 1295, 1150, 1085, 1000, 950, 850. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.13 (s, 6H), 2.17 (s, 3H), 2.35 (s, 9H), 2.62 (s, 3H), 6.79 (s, 1H), 6.95 (s, 2H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 10.95, 11.40, 18.85, 19.01, 20.02, 21.29, 117.30, 125.56, 125.73, 127.50, 127.89, 128.16, 128.32, 131.75, 138.92, 139.20, 150.20, 154.25. – MS (EI, 70 eV): *m/z* (%) = 292 (100), 277 (48), 262 (12), 247 (8), 131 (10).

$C_{21}H_{24}O$ (292.4) Calcd. C 86.25 H 8.27
Found C 86.03 H 8.10

4,6,7-Trimethyl-3-phenylbenzofuran (**22**) *and 3-Mesitylbenzofuran* (**23**): According to the general procedure for enol oxidation with the acetonitrile replaced by dichloromethane 50.4 μmol of **9** was treated with 108.4 μmol of **14**. According to a quantitative ^{1}H-NMR analysis with *m*-nitroacetophenone as standard and GC-MS study the two isomeric benzofurans were formed in 12% (**22**) and 27% (**23**) yields, respectively, besides a remainder of 12% of recovered **9**. We were unable to separate the two benzofurans by liquid chromatography or gas chromatography. – Data for **22**: ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.05 (s, 3H), 2.28 (s, 3H), 2.31 (s, 3H), 6.74 (s, 1H), 7.20–7.24 (m, 5H), 7.90 (s, 1H). – **23**: ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.27 (s, 6H), 2.29 (s, 3H), 6.87 (s, 2H), 7.30 (m$_c$, 2H), 7.50 (m$_c$, 2H), 7.87 (s, 1H). – Mixture of **22** and **23**: MS (EI, 70 eV): *m/z* (%) = 236 (100) [M$^+$], 221 (60), 192 (20), 178 (24), 143 (20), 95 (22), 89 (32), 76 (18).

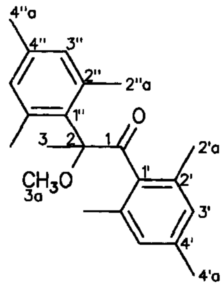
Oxidation Reactions with Incorporation of Nucleophiles

4-Mesityl-2-methyl-5-phenyloxazole (**20**): The reaction of 55.5 μmol of enol **9** with 200 mol-% of **14** according to the general procedure for enol oxidation afforded 68% of pure **20** (purity >99.8%). – IR (CCl$_4$): = 3060 cm^{-1}, 2910, 2850, 1700, 1600, 1440, 1375, 1290, 1220, 1055, 1030. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.04 (s, 6H), 2.31 (s, 3H), 2.57 (s, 3H), 6.91 (s, 2H), 7.17–7.30 (m, 5H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.17, 20.02, 21.27, 123.90, 127.49, 127.53, 128.39, 128.53, 128.73, 128.86, 129.00, 129.84, 138.12, 160.06. – MS (EI, 70 eV): *m/z* (%) = 277 (62) [M$^+$], 235 (100), 220 (70), 192 (38), 178 (32), 158 (12), 131 (16), 115 (22), 77 (50).

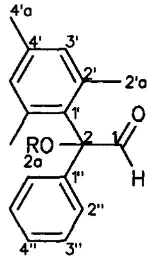
$C_{19}H_{19}NO$ Calcd. 277.1466 Found 277.1465

1,2-Dimesityl-2-methoxypropanone (**25**): The reaction of 51.0 μmol of enol **8** with 200 mol-% of **14** according to the general procedure for enol oxidation in the presence of methanol yielded 27% of **25** and 54% of **24**. After chromatography on silica gel with dichloromethane/hexane (2:1) as eluent pure **25** (purity >95.7%, R_f = 0.38) was obtained. – IR (NaCl): $\tilde{\nu}$ = 2890 cm^{-1} (CH), 1675 (CO), 1595 (C=C), 1430. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 1.83 (s, 6H), 2.09 (s, 3H), 2.21 (s, 3H), 2.25 (s, 3H), 2.29 (s, 6H), 3.14 (s, 3H), 6.74 (s, 2H), 6.77 (s, 2H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 19.9 (C-3), 20.46 (C-4″a), 21.10 (C-4′a), 23.99 (C-2″a), 25.21 (C-2′a), 50.10 (C-2a), 90.42 (C-2), 128.11 (C-3″), 132.56 (C-3′), 133.28 (C-4″), 134.83 (C-2″), 136.85 (C-2′), 137.92 (C-4′), 138.12 (C-1″), 139.56 (C-1′), 208.66 (C-1). – MS (EI, 70 eV): *m/z* (%) = 177 (100), 147 (14), 43 (65). – MS (CI, NH$_3$): *m/z* (%) = 342 (6) [M + NH$_4^+$], 310 (16), 293 (100) [M$^+$ – CH$_3$O].

$C_{12}H_{17}O$ [M$^+$ – $C_{10}H_9O$] Calcd. 177.1279 Found 177.1276



25



26 (R : CH$_3$)
27 (R : H)

2-Mesityl-2-methoxy-2-phenylacetaldehyde (**26**): The reaction of enol **9** according to the general procedure in the presence of methanol afforded **26** in 57% yield. Pure **26** (purity >99.0%) was isolated after chromatography on silica gel (dichloromethane/hexane, 2:1; R_f = 0.60). – IR (NaCl): $\tilde{\nu}$ = 2900 cm^{-1} (CH), 2810 (CHO), 1710 (CO), 1600 (C=C). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.09 (s, 6H), 2.27 (s, 3H), 3.37 (s, 3H), 6.82 (s, 2H), 7.14–7.29 (m, 5H), 9.73 (s, 1H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.76 (C-4′a), 23.07 (C-2′a), 52.74 (C-2a), 127.54 (C-2″), 127.85 (C-3″), 127.95 (C-4″), 128.75 (C-3′), 131.36 (C-2′), 132.30 (C-1′), 138.34 (C-1″), 139.02 (C-4′), 139.13 (C-2), 194.39 (C-1). – MS (EI, 70 eV): *m/z* (%) = 239 (100) [M$^+$ – CHO], 163 (22), 91 (18), 77 (26), 44 (12). – MS (CI, NH$_3$): *m/z* (%) = 286 (100) [M + NH$_4^+$], 268 (18) [M$^+$], 237 (6), 209 (25).

$C_{17}H_{19}O$ [M$^+$ – CHO] Calcd. 239.1436 Found 239.1438

2-Hydroxy-2-mesityl-2-phenylacetaldehyde (**27**): Oxidation of enol **9** according to the general procedure in the presence of water afforded **27** in 57% yield. Isolation after chromatography on silica gel (dichloromethane/hexane, 2:1; R_f = 0.57) afforded pure **27** (purity >98.5%). – IR (NaCl): $\tilde{\nu}$ = 3450 cm^{-1} (s, OH), 2900 (CH), 2810 (CHO), 1700 (CO), 1600 (C=C). – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.07 (s, 6H), 2.26 (s, 3H), 4.80 (s, 1H, OH), 6.82 (s, 2H), 7.14–7.29 (m, 5H), 9.82 (s, 1H). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 20.73 (C-4′a), 23.27 (C-2′a), 127.01 (C-2″), 128.03 (C-4″), 128.40 (C-4′), 129.06 (C-3″), 131.31 (C-3′), 136.02 (C-1′), 137.61 (C-1″), 138.07 (C-2′), 140.03 (C-2), 196.22 (C-1). – MS (EI, 70 eV): *m/z* (%) = 147 (100) [$C_{10}H_{11}O^+$], 119 (22), 105 (19), 91 (19), 77 (16), 51 (10). – MS (CI, NH$_3$): *m/z* (%) = 272 (100) [M + NH_4^+], 254 (10) [M^+].

$C_{10}H_{11}O$ [$M^+ - C_7H_7O$] Calcd. 147.0809 Found 147.0812

Synthesis of 5-Mesityl-2-methyl-4-phenyloxazole (**21**): 2-Chloro-1-mesityl-2-phenylethanone was synthesized according to a procedure described by Masilamani and Rogic[50]. The product (23%) was purified by chromatography over silica gel with dichloromethane as eluent. For the synthesis of **21** a procedure described by Lora-Tamayo was adapted[24]: To 2.0 g (7.3 mmol) of 2-chloro-1-mesityl-2-phenylethanone was added 0.29 g (7.3 mmol) of acetonitrile and 1.8 (7.3 mmol) of tin tetrachloride under nitrogen. The mixture was stirred at 25°C for 18 h and at 100°C for 3 h. The black residue was dissolved in ethyl acetate, and after extraction with brine, dried with sodium sulfate. After solvent removal 2.0 g of crude product was obtained, that could be purified by chromatography over silica gel using dichloromethane to afford 13% of oxazole **21** (purity >99.0%). – IR (CCl$_4$): $\tilde{\nu}$ = 3060 cm^{-1}, 2900, 1600, 1430, 1260, 1055, 1150. – ^{1}H NMR (250 MHz, CDCl$_3$): δ = 2.06 (s, 6H, *o*-CH$_3$), 2.34 (s, 3H, *p*-CH$_3$), 2.54 (s, 3H, CH$_3$C=N), 6.96 (s, 2H, H-Mes), 7.17–7.27 (m, 2H, H-Ph), 7.43–7.5 (m, 3H, H-Ph). – ^{13}C NMR (100 MHz, CDCl$_3$): δ = 14.08, 19.95, 21.36, 125.49, 127.34, 128.30, 128.60, 128.67, 129.50, 132.03, 135.60, 138.80, 139.70, 160.74. – MS (EI, 70 eV): *m/z* (%) = 277 (60) [M^+], 235 (100), 220 (60), 192 (40), 178 (30), 158 (12), 131 (16), 115 (20), 77 (40), 51 (20), 43 (24).

$C_{19}H_{19}NO$ Calcd. 277.1466 Found 277.1468

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[1] Enol Cation Radicals in Solution, Part 3; Part 2 see ref.[4]

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