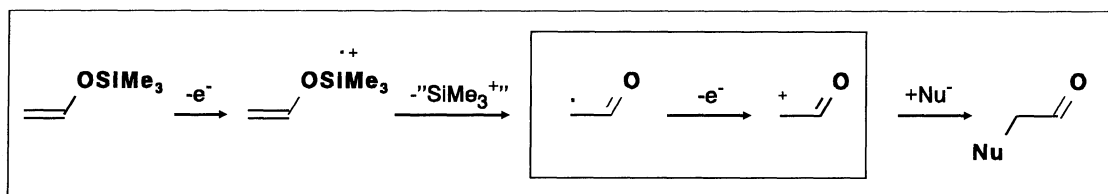


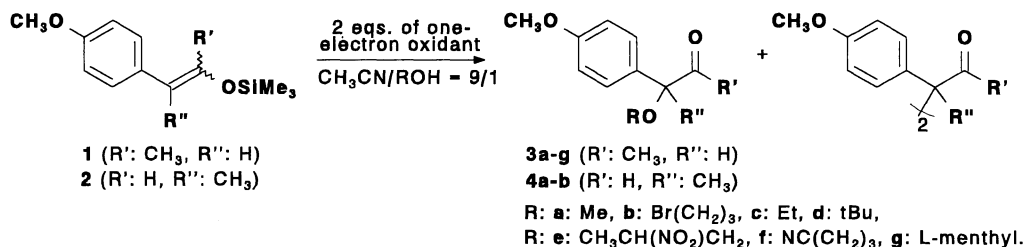
α -Umpolung of Ketones and Aldehydes via the Corresponding Silyl Enol Ether Cation Radicals¹⁾Michael SCHMITTEL^{*,†} and Michael LEVISInstitut für Organische Chemie und Biochemie der Universität Freiburg,
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The α -Umpolung of ketones and aldehydes via their silyl enol ether cation radicals has been developed and tested for the use of different nucleophiles.

Our experience with the recently developed α -Umpolung of ketones via the corresponding enol cation radicals,¹⁾ necessitating the extensive control of two oxidation steps with quite often conflicting requirements on the oxidant, initiated the present study of the one-electron oxidation of silyl enol ethers. Since silyl enol ether cation radicals²⁾ are known to form α -carbonyl radicals³⁾ after C-Si bond cleavage, we reasoned, that in case of electron-rich radicals⁴⁾ a further one-electron oxidation should follow. Interestingly, this straightforward approach to α -carbonyl cation chemistry has not been studied, yet.



In contrast to other α -Umpolung strategies for ketones starting from silyl enol ethers that make an electron-rich enol component react with an electropositive oxygen source,⁵⁾ this new approach via α -carbonyl cations allows to introduce polyfunctional nucleophiles in one step. Since the nucleophiles have to withstand the oxidative conditions, we have first turned our attention to alcohols. Importantly, this new α -substitution also works for aldehydes, a reaction not often realized in literature.⁶⁾



When we reacted the electron-rich silyl enol ethers **1** or **2** in the presence of alcohols with various one-electron oxidants, indeed the α -substituted products **3a-g** and **4a,b** were obtained, demonstrating the feasibility of our approach. With **1** we observed oxidative dimerization of the silyl enol ether as a side route, a well documented reaction of less sterically hindered systems.⁷⁾

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Table 1. Yields in the α -Umpolung via Silyl Enol Ethers **1** or **2** in Anhydrous Acetonitrile Using Different Nucleophiles and One-electron Oxidants.

Silyl enol ether	Nucleophile ROH	One-electron oxidant ^{a)}	Addition time/ min	α -Umpolung product (Yield/ %)	Dimer yield/ %
1	MeOH	TTA⁺	2	3a (56)	--
1	MeOH	CAN	im ^{b)}	3a (34)	--
1	3-bromopropanol	CAN	4	3b (67)	--
1	EtOH	FePhen	im ^{b)}	3c (53)	2
1	<i>t</i> BuOH	TTA⁺	im ^{b)}	3d (23)	15
1	CH ₃ CH(NO ₂)CH ₂ OH	CAN	4	3e (48)	50
1	NCCH ₂ CH ₂ CH ₂ OH	CAN	4	3f (11)	10
1	L-menthol	CAN	4	3g (53)	39
1	L-menthol	FePhen	4	3g (76)	7
2	MeOH	FePhen	im ^{b)}	4a (80)	--
2	MeOH	CAN	im ^{b)}	4a (80)	--
2	MeOH	Cu(OTf) ₂	im ^{b)}	4a (71)	--
2	3-bromopropanol	CAN	im ^{b)}	4b (98)	--
2	3-bromopropanol	FePhen	im ^{b)}	4b (77)	--

a) **TTA⁺**: tri(*p*-tolyl)aminium hexafluoroantimonate, **CAN**: Ce(NH₄)₂(NO₃)₆, **FePhen**: tris-(1,10-phenanthroline)iron(III) hexafluorophosphate, for details see Ref. 1 and 8. b) Immediate addition of the whole amount of the silyl enol ether.

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