

ELECTRON-RICH ALKYL OLEFINS AND THEIR RADICAL CATIONS^{1,2}

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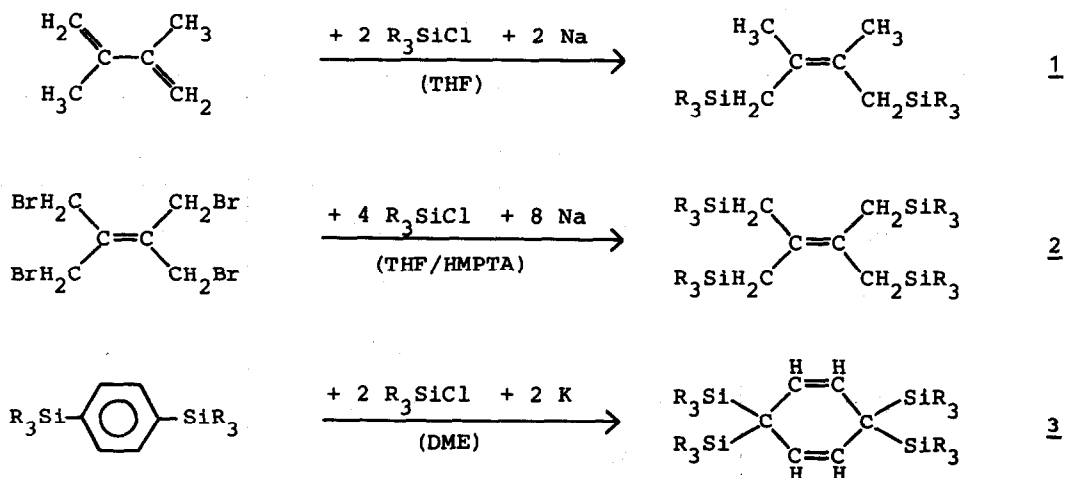
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Molecules exhibiting first ionization potentials below ~8 eV can in general be oxidized to their radical cations in solution. One of the principles to design those compounds consists of multiple introduction of R₃Si substituents in β position to π systems or lone pairs¹. The resulting strong electron donation³ is best rationalized by C-Si hyperconjugation⁴.

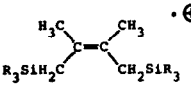
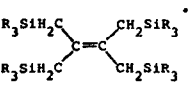
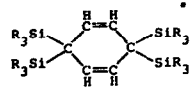
The olefins Z-1,4-bis(trimethylsilyl)-2,3-dimethyl-2-butene 1, 1,4-bis(trimethylsilyl)-2,3-bis(trimethylsilylmethyl)-2-butene 2 and 3,3,6,6-tetrakis(trimethylsilyl)-1,4-cyclohexadiene 3 have been synthesized by the following procedures⁵ (R = CH₃) :



The compounds 1 - 3 display remarkable molecular properties. For instance, their first vertical ionization potentials amount to only 7.70 eV (1), 7.15 eV (2) and 7.00 eV (3); values, which are merely exceeded by dialkylamino substituted derivatives⁶. Accordingly, the $\pi \rightarrow \pi^*$ transitions are bathochromically shifted e.g. to 42000 cm^{-1} (hexane, $\epsilon_{\text{mol}} 6000$) for 2, i.e. 1 eV relative to other tetraalkyl ethylenes⁷.

The exceptional stabilization of the radical cation ground state in the gas phase as demonstrated by the low first ionization potentials suggests that these olefins might form a "persistent"⁸ radical cation also in solution. Corroborative evidence results upon addition of tetracyanoethylene (TCNE) to 2 and 3 in H_2CCl_2 : instead of the usual olefin charge transfer complex formation a complete charge exchange occurs according to the developing esr signals of the TCNE radical anion. No counterion could be detected, however, the radical cations can be generated separately by one-electron oxidation with aluminum chloride in dichloromethane.

The well-resolved esr spectra (Figure 1) reveal inequivalency of the methylene protons in 1^{•+} and 2^{•+}. Computer simulation (Figure 2) of the hyperfine splitting with e.g. 2775 lines for 2^{•+} has been achieved using the following parameters ($R = \text{CH}_3$):

esr coupling constants (mT)			
$a_{\text{H}}^{\text{SiCH}_3}$	0.046	0.031	0.018
$a_{29\text{Si}}$	~ 1.4	1.27	2.09
$a_{\text{H}_a}^{\text{CH}_2}$	1.070	0.855	
$a_{\text{H}_b}^{\text{CH}_2}$	0.760	0.730	
$a_{\text{H}}^{\text{CH}_3}$	1.070		
a_{H}^{CH}			0.303
line width (mT)	0.015	0.020	0.006

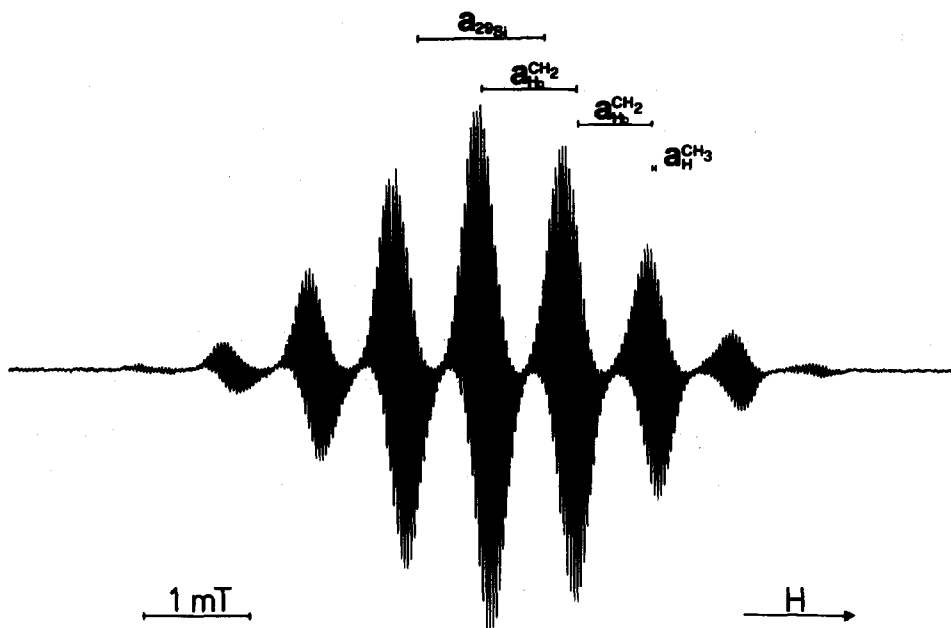


FIGURE 1. ESR spectrum of the radical cation of 1,4-bis(trimethylsilyl)-2,3-bis(trimethylsilylmethyl)-2-butene 2

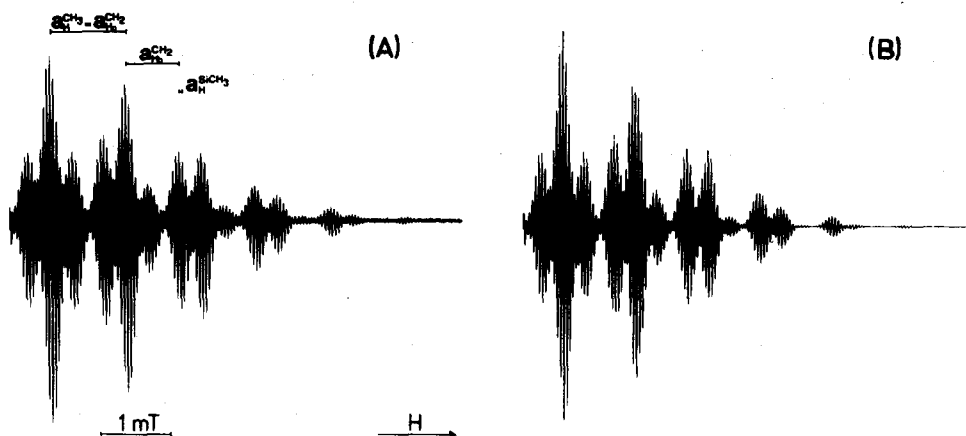


FIGURE 2. ESR spectrum of the radical cation of Z-1,4-bis(trimethylsilyl)-2,3-dimethyl-2-butene 1 : high-field half (A) and its computer simulation (B)

The differing coupling constants $a_{\text{H}_a}^{\text{CH}_2} \neq a_{\text{H}_b}^{\text{CH}_2}$ indicate considerably restricted $-\text{CH}_2\text{SiR}_3$ rotation on the esr time scale in $\underline{1}^{\bullet\oplus}$ and $\underline{2}^{\bullet\oplus}$.

For $\underline{3}^{\bullet\oplus}$ one deduces from the McConnell relation $g_{\text{C}}^{\pi} = a_{\text{H}}^{\text{CH}}/|p_{\text{d}}|$ assuming $|p_{\text{d}}| \sim 3$ mT a total π spin population of $\sum g_{\text{C}}^{\pi} \sim 0.4$. The extensive spin delocalization on to the silyl substituents is further substantiated by the relatively large coupling constants $a_{29\text{Si}}$ and $a_{\text{H}}^{\text{SiCH}_3}$ for all three radical cations.

The above procedure - i.e. design of molecules with low ionization potentials determined by pe spectroscopy, in combination with appropriate one-electron oxidation methods accompanied by esr characterization^{1,9} - has allowed to establish the existence of numerous other radical cations containing boron, carbon, silicon, tin, nitrogen, phosphorus, arsenic, sulfur and selenium^{1,9,10}.

REFERENCES AND NOTES

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- ¹⁰ Unpublished results in cooperation with G.Fritz, R.Gleiter, H.Nöth, H.Sakurai, D.Seebach and N.Wiberg.