



Radical Anions of Acyclic Vicinal Oligoketones: An Electron Spin Resonance Study

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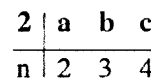
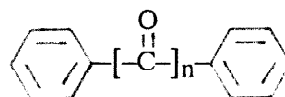
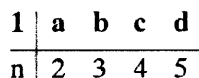
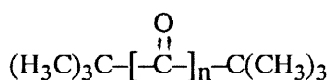
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Abstract: Radical anions of acyclic vicinal oligoketones with up to five CO units, **1a-d^{•−}** and **2a-c^{•−}**, were generated by reduction of the parent compounds with potassium in presence of kryptofix® 222 and studied by ESR measurements. The inverse correlation between *g*-values and the amount of spin populations on the terminal substituents prove that these radical anions are extended π -systems.

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Linking adjacent carbonyl groups leads to vicinal oligoketones.¹ These compounds deserve interest because of their structures, their reactivity and their electronic properties as a function of the number of CO-groups. A study of their electronic absorption spectra and their reduction potentials shows² a decrease of the energy of the long wavelength band and of the reduction potential with an increasing number of CO-groups. In the latter case the reversible reduction potential dropped from benzil (−1.25 V) to diphenylpentaketone (−0.27 V) by nearly 1 V. The relatively low values suggested to us a study of the radical anions of the di-*tert*-butyl **1b-d** and the diphenyl vicinal oligoketones **2b-c** of ESR spectroscopy. The compounds were either available in our laboratory or were prepared following literature procedures.^{2–6}



To our knowledge from acyclic vicinal oligoketones only the radical anions of diphenyltriketone (**2b**)⁷ and bis(2,4,6-trimethylphenyl)tetraketone⁸ have been reported. In dimethyl sulfoxide solution⁷ or in the presence of cryptands⁸ these radical anions exist as free ions. Since **2b^{•−}** was only somewhat persistent (30 min) under the experimental conditions, we followed the procedure of H. Bock et al.⁸ and reduced **1a-d** and **2a-c** in 1,2-dimethoxyethane (DME) with a potassium mirror in the presence of kryptofix® 222 to inhibit possible ion pairing. The radical anions were readily generated by this procedure and were sufficiently long lived to perform ESR studies. All results obtained, i.e. the isotropic hyperfine coupling (hfc) constants and *g*-values are collected in Table 1. The ESR spectra of **1b^{•−}**, **1c^{•−}**, and **1d^{•−}** are shown in Figure 1, and the ESR spectra of **2b^{•−}** and **2c^{•−}** in Figures 2 and 3, respectively. The radical anions **1a^{•−}**⁹ and **2a^{•−}**¹⁰ of the

α -diketones were also included in this study. Their data obtained under identical experimental conditions allow for a direct comparison.

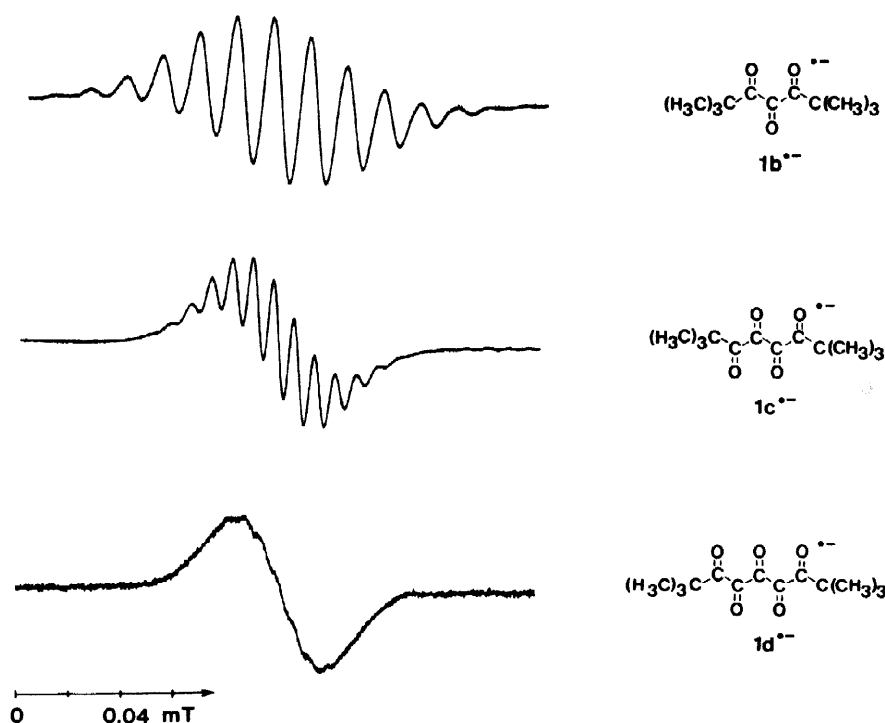


Figure 1. ESR spectra of $1b^{\bullet-}$ at 300 K, $1c^{\bullet-}$ at 265 K, and $1d^{\bullet-}$ 240 K in DME/kryptofix® 222.

Table 1. Isotropic Hyperfine Coupling Constants and g -Values of the Radical Anions $1a^{\bullet-}$ and $2a-c^{\bullet-}$ in DME/kryptofix® 222.

	T/K	$a(H, t\text{-bu})/mT$	$a(H_o)/mT$	$a(H_m)/mT$	$a(H_p)/mT$	$g\text{-Value}^a$
$1a^{\bullet-}$	300	0.027 (18H) ^b				2.0050
$1b^{\bullet-}$	300	0.014 (18H) ^b				2.0053
$1c^{\bullet-}$	265	0.008 (18H)				2.0055
$1d^{\bullet-}$	240	0.0063 (18H)				2.0058
$2a^{\bullet-}$	300		0.101 (4H) ^b	0.034 (4H) ^b	0.115 (2H) ^b	2.0050
$2b^{\bullet-}$	300		0.060 (4H) ^b	0.019 (4H) ^b	0.060 (2H) ^b	2.0052
$2b^{\bullet- c}$	230		-0.061 (4H) ^b	+0.019 (4H) ^b	-0.065 (2H) ^b	
$2c^{\bullet-}$	260		0.017 (4H)	0.006 (4H)	0.017 (2H)	2.0056

a. ± 0.0001 . b. ± 0.001 mT. c. ENDOR and triple resonance studies.

The ESR results of $1a^{\bullet-}$ (Table 1) agree well with literature data.^{9a} Also the higher homologues $1b^{\bullet-}$ and $1c^{\bullet-}$ show in their ESR spectra (Figure 1) a clear hyperfine structure representing 18 hydrogens. In the ESR spectrum of $1d^{\bullet-}$ (Figure 1), however, this hyperfine structure is only weakly indicated. The “lower“

resolution with increasing chain length may be caused in part by the small magnitude of the hfc splittings. A more plausible explanation, however, would be that with higher chain length ($n = 4$, $n = 5$) an equilibrating mixture of *all-trans* (shown in Figure 1) and *trans-cis* isomers in the ESR spectra is observed. The steric requirements of the *tert*-butyl groups force $1a^{\bullet-}$ into an exclusive *trans* arrangement.^{9d} This can also be assumed for $1b^{\bullet-}$, but not for the higher homologues. Moreover, different arrangements of the cryptand enclosed cation with regard to the radical anion in the range of the ESR time scale may contribute to the observed line broadening.

As expected, the radical anions become less persistent with increasing chain length. Therefore, the ESR measurements of $1c^{\bullet-}$ and $1d^{\bullet-}$ had to be performed at lower temperatures. Interestingly, the ESR spectrum of $1d^{\bullet-}$ changes at 240 K within 30 min and is replaced by that of $1c^{\bullet-}$ formed by CO extrusion.

Like the ESR data of $2a^{\bullet-}$ ¹⁰ and $2b^{\bullet-}$ ⁷, which agree closely with those reported in the literature, the ESR results of the higher homologue $2c^{\bullet-}$ clearly show an equal interaction of the unpaired electron with both phenyl substituents. In case of $2b^{\bullet-}$ it was possible to obtain an ENDOR spectrum, and triple resonance studies¹¹ provided the relative signs of the hfc splittings and their assignment. The ESR spectra of $2b^{\bullet-}$ and $2c^{\bullet-}$ are shown for comparison in Figures 2 and 3, respectively. Also in this series a distinct line broadening in the ESR spectrum of $2c^{\bullet-}$ (Figure 3) was observed.

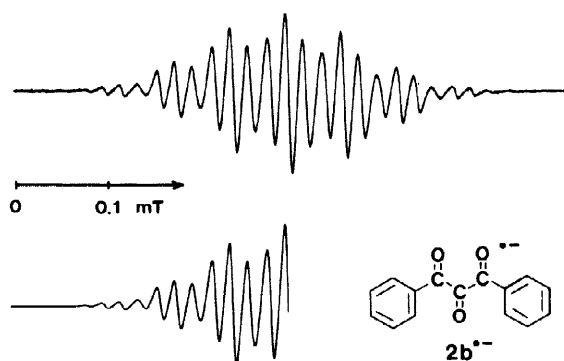


Figure 2. ESR spectrum of $2b^{\bullet-}$ in DME/kryptofix® 222 at 300 K together with a simulation using the data given in Table 1.

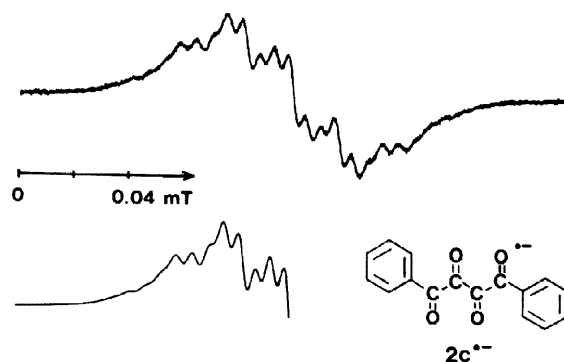


Figure 3. ESR spectrum of $2c^{\bullet-}$ in DME/kryptofix® 222 at 260 K together with a simulation using the data given in Table 1.

Our work demonstrates that radical anions of acyclic vicinal oligoketones can be generated and detected by ESR with up to five carbonyl units in the chain. According to the observed ESR hyperfine structure, the unpaired electron interacts equally with both terminal substituents. All radical anions are delocalized species. With an increasing CO-chain the magnitudes of the corresponding hfc splittings decrease considerably, in the *tert*-butyl series from 0.027 ($1a^{\bullet-}$) to 0.0063 mT ($1d^{\bullet-}$). Each elongation of the CO-chain shifts spin population from the terminal substituents into the extended π -system. This is confirmed by the continuous and distinct increase of the g -values ($1a^{\bullet-}$: 2.0050; $1d^{\bullet-}$: 2.0058). The increase of the g -values is related to growing spin-orbit coupling due to the interaction of the unpaired electron with the lone-pairs at the oxygen atoms. The inverse correlation between g -values and the amount of spin population on the terminal substituents prove that the unpaired electron in these radical anions up to five CO units is fully delocalized.

Experimental

ESR and ENDOR studies were performed on a Bruker ESP 300 spectrometer equipped with the ER 252 (ENMR) ENDOR system. *g*-Values were determined using an NMR gaussmeter and a Hewlett-Packard 5342A microwave frequency counter; this was calibrated with the perylene radical cation. Hyperfine coupling constants measured in megahertz (ENDOR) were converted into millitesla using $1 \text{ MHz} = 0.07145/g_{\text{ex}} \text{ mT}$.

The radical anions were generated by reduction of the parent compounds (about 1 mg) in 1,2-dimethoxyethane (DME) (about 1 ml) with potassium under high-vacuum conditions in the presence of kryptofix® 222 Merck (1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo[8.8.8]hexacosane; about 4 mg). The solvent was carefully dried (potassium) and deoxygenated. Potassium was purified by repeated vacuum distillation.

Acknowledgements

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References and Notes

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