

OXIDATION OF FERROCENYL KETONES

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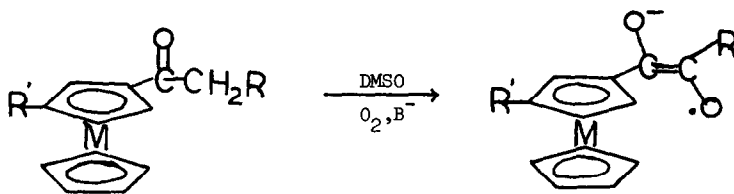
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Ketones with an α methylene group can be oxidized with molecular oxygen to the corresponding semidiones in dimethylsulfoxide (DMSO) solution containing an excess of potassium *t*-butoxide. This reaction is quite general and many semidiones prepared by this technique have been observed by esr spectroscopy (1,2). Metallocene semidiones have not previously been observed and this class of semidione is unusual, in that, overoxidation produces a paramagnetic species consistent with ortho oxygenation of the metallocene ring.

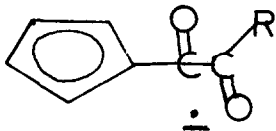
Ketones I-VI are oxidized initially to semidiones Ia-VIa (Table I), whose esr spectra indicate a very small amount of spin delocalization into the metallocene ring.



	M	R	R'		a^H in gauss	g
I	Fe	CH ₃	H	Ia	4.20(3H), 0.51(2H)	2.00706 _± .00001
II	Ru	CH ₃	H	IIa	4.25(3H), 0.54(2H)	2.00642
III	Fe	CH ₃	\bar{n} -butyl	IIIa	4.20(3H), 0.50(2H)	2.00706
IV	Fe	CH ₂ CH ₃	H	IVa	3.80(2H), 0.50(2H)	2.00706
V	Fe	CH(CH ₃) ₂	H	Va	1.75(1H), 0.50(2H)	2.00706
VI	Fe	∅	H	VIa	1.70(3H), 0.50(4H)	2.00666

Table I

Hyperfine splitting constants (hfsc) calculated from spin densities obtained by the Huckel-McLachlan method (3) using π system VII agree essentially with the experimental hfsc.



VII

These semidiones have some what high g values (4). An interesting observation is that $g_{IIa} < g_{Ia}$ an order opposite to that of the spin-orbit, LS, coupling constants for the metals involved ($\zeta_{Ru^{+2}} = 1140 \text{ cm}^{-1}$, $\zeta_{Fe^{+2}} = 410 \text{ cm}^{-1}$). These results imply very little free electron density at the metal atom itself and this conclusion is supported by the absence of metal hyperfine splitting (Fe^{57} , spin = 1/2, 2.245% natural abundance, Ru^{99} , spin = 5/2, 12.81% natural abundance, or Ru^{101} , spin = 5/2, 16.98% natural abundance).

The metal apparently plays a more subtle role in its effect on the g value, perhaps by altering molecular orbital energy levels through E_{1g} (ring E_{1g} - metal $d_{xy, yz}$) or E_{2g} (ring E_{2g} - d_{xy, x^2-y^2}) ring-metal interaction so that the electron of a Ia is in a higher energy orbital (5,6). This matter will be discussed in detail elsewhere. For the present purpose, it is simply necessary to point out that the difference in g value between Ia and IIa constitutes proof that the metallocene moiety is intact.

Another unusual property of this class of semidione is the remarkably slow rate of hydrogen-deuterium exchange of the alkyl hydrogens α to the semidione when the oxidation is conducted in $DMSO-d_6$ (4), Table II. This slow exchange rate is consistent with the electron supplying property of the metallocene ring.

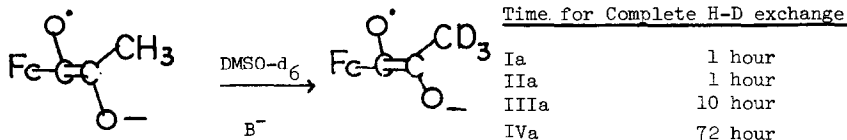
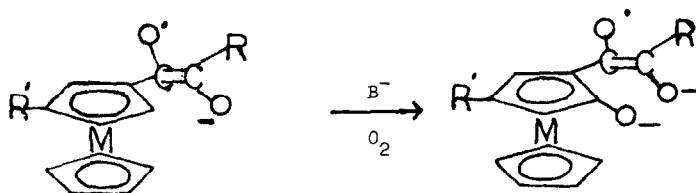


Table III

An additional amount of oxygen results in the disappearance of semidiones Ia-Va and the appearance of new, but similar, paramagnetic species. These new substances (figure 1) have properties consistent with structures Ib-Vb (Table III).



	<u>a</u>	<u>H</u> <u>a</u> in gauss	<u>b</u>	<u>g</u>
Ia	Ib	4.25(3H), 0.50(3H)		2.00708+ .00001
IIa	IIb	4.30(3H), 0.55(3H)		2.00644
IIIa	IIIb	4.24(3H), 0.55(4H)		2.00708
IVa	IVb	3.70(2H), 0.50(3H)		2.00708
Va	Vb	1.71(1H), 0.50(3H)		2.00708

Table III

When this overoxidation is conducted in DMSO- d_6 before hydrogen-deuterium exchange can occur in Ia-Va, spectra Ib-Vb are observed to be identical to those produced in ordinary DMSO; this results, as well as entry IIIb of Table III, requires that the additional hydrogen splitting observed in Ib, IIb, IVb, and Vb originate in the metallocene ring. In DMSO- d_6 the exchange of the alkyl hydrogens with deuterium in Ib-Vb is very slow (less than 20% after 5 hours for Ib), and this reduction in the rate of hydrogen-deuterium exchange is in accord with the presence of an electron supplying substituent on the metallocene ring.

The expected chemical reactivity as well as Huckel-McLachlan calculations are in agreement with ortho as opposed to meta oxygenation of the metallocene ring. This study represents the first example of direct oxygenation of a metallocene ring.

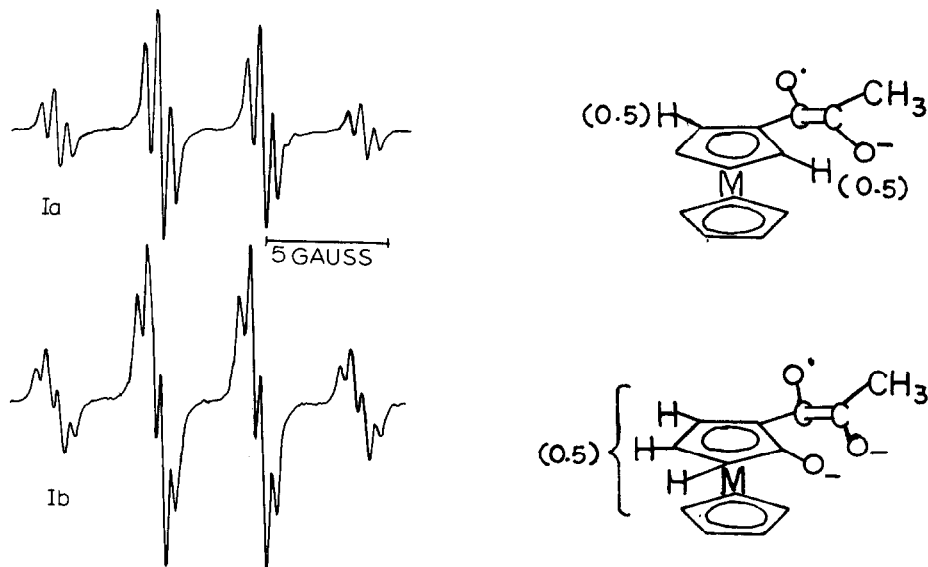


Figure 1. The high resolution esr spectra of Ia and Ib.

1. This work was supported by The Petroleum Research Fund administered by The American Chemical Society (Grant 1375-G1).
2. G. A. Russell, et al., *Record of Chemical Progress*, 27, 3(1966).
3. A. D. McLachlan, *Mol. Phys.*, 3, 233(1960).
4. The semidione derive from propiophone has a g value of 2.00510. The g values were determined with a Magnion-Model G502- gaussmeter and a Hewlett-Packard-Model 5253B-frequency converter. The three α hydrogens are replaced with deuterium in less than one minute.
5. A. J. Stone, *Mol. Phys.*, 6, 509(1963).
6. H. P. Fritz, "Advances in Organometallic Chemistry", edited by F. G. A. Stone and R. West, Vol. 1, Academic Press, N.Y., 1964, pp. 239. The C-M bond is stronger for M=Ru than for M=Fe as indicated by the IR stretching frequency of 478 cm^{-1} for Fe-C and 381 cm^{-1} for Ru-C.