Tetrahedron Letters No. 47, pp 4573 - 4576, 1971. Pergamon Press. Printed in Great Britain.

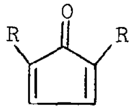
REDUCTION OF CONJUGATED UNSATURATED KETONES TO RADICAL ANIONS BY DIMETHYL SULFOXIDE SOLUTIONS OF POTASSIUM <u>tert</u>-BUTOXIDE

Glen A. Russell and Ronald L. Blankespoor

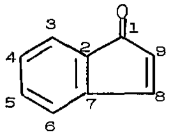
Department of Chemistry, Iowa State University, Ames, Iowa 50010

(Received in USA 1 October 1971; received in UK for publication 25 October 1971)

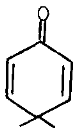
Electrolytic reduction of α,β-unsaturated ketones in dimethylformamide has yielded radical anions (ketyls) observed by electron spin resonance (esr) spectroscopy.[1] We were surprised to find that (I) - (VI) were reduced to their radical anions by dimethyl sulfoxide (DMSO) solutions of potassium *tert*-butoxide. Since the lifetimes of $(I\cdot^-)$ - $(VI\cdot^-)$ were only several minutes or less it was necessary to continually mix flowing DMSO solutions of the ketones (0.04 M) with DMSO solutions of potassium *tert*-butoxide (0.08 M) at the entrance of the esr cell so that ∼0.1 sec. elapsed between mixing and esr detection.†



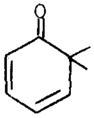
(I) a; R=H
b; R=D



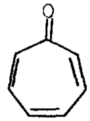
(II)



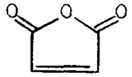
(III)



(IV)



(V)



(VI)

---

†A quartz cell of ∼0.05 ml volume between the point of mixing and detection was used (Varian Associates V-4549A) with flow rates of 5-10 ml/sec. Spectra were recorded with a Varian V-4502 spectrometer using sweep rates of ∼5 gauss/-min.

Since (Ia) and (Ib) are non-isolable at room temperature,[2] these ketones were generated in situ from 4-bromo-2-cyclopentenone[3] and 2,5,5-trideuterio-4-bromo-2-cyclopentenone (2,5,5-trideuterio-2-cyclopentenone was prepared from 2,2,5,5-tetradeuteriocyclopentanone by the method of Garbisch[4]). The hyperfine splitting constants (hfsc's) obtained from the esr spectra of (Ia•$^-$) (Figure) and (Ib•$^-$) are assigned in Table 1. These assignments are in excellent agreement with Hückel and McLachlan[5] MO calculations. The lifetime of (I•$^-$) in DMSO solution at room temperature was ~5-10 seconds.

Table 1. Observed hyperfine splitting (G) and calculated spin densities

Position	Observed hfsc, a^H (Ia•$^-$)	(Ib•$^-$)	Calculated spin densities Hückel	McLachlan
C-1			0.2355	0.2515
C-2	2.91	0.46(a^D)	0.1164	0.0905
C-3	5.27	5.27	0.1770	0.2022
O			0.1779	0.1630

[a] $\beta_{C=O} = 1.4\ \beta_{CC}$; $\alpha_O = \alpha_C + 1.8\ \beta_{CC}$.

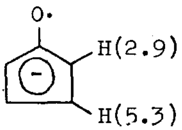
Although electrolytic reduction of (II) gave a polymer without an esr signal,[1] reaction of 3-bromo-1-indanone[6] with basic DMSO solution gave an esr signal of (II•$^-$) (Figure). The assignment of hfsc's is made in Table 2 on the basis of calculated spin densities. The lifetime of (II•$^-$) in DMSO at room temperature was several minutes.

Table 2. Observed hyperfine splitting (G) and calculated spin densities for (II•$^-$)

Position	Observed hfsc, a^H	Calculated spin densities Hückel	McLachlan
C-1		0.2248	0.2601
C-2		0.0609	0.0696
C-3	0.91	0.0551	0.0313
C-4	1.94	0.0586	0.0599
C-5	1.50	0.0574	0.0463
C-6	1.15	0.0563	0.0455
C-7		0.0597	0.0555
C-8	7.10	0.2296	0.3209
C-9	0.20	0.0645	0.0090
O		0.1330	0.1210

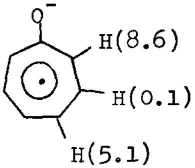
The hfsc's obtained from the esr spectra of $(\mathrm{III}^{\cdot -})$ and $(\mathrm{IV}^{\cdot -})$ in DMSO solution were in agreement with those previously reported.[1] Although room temperature electrolytic reduction of (V) failed to give an esr signal,[1] $(\mathrm{V}^{\cdot -})$ was observed at room temperature by reduction with basic DMSO solution. The hfsc's of tropone ketyl in DMSO were in agreement with those reported previously by Ikegami and Seto.[7] Maleic anhydride, (VI), gave a spectrum of a triplet with $a^H = 6.79$ G upon reduction in basic DMSO solution.† This is consistent with the 6.1 gauss coupling observed for the hydrogens in dimethylmaleic anhydride radical anion by Nelsen and Seppanen.[8]

Interestingly, the hfsc's of cyclopentadienone ketyl are significantly lower than those observed for tropone ketyl.[7] This possibly results from the enhanced resonance contributions of structures (VII) and (VIII) rather than structures (IX) and (X) which would be expected to possess less aromatic character.



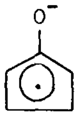
$\Sigma \underline{a}^H = 16.4$

(VII)

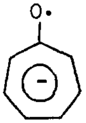


$\Sigma \underline{a}^H = 27.6$

(VIII)



(IX)



(X)

Attempts to reduce N-methyl-2-pyridone, 4-pyrone, 2,6-dimethyl-4-pyrone and phthalic anhydride with basic DMSO under flow conditions failed to give esr signals. Similar attempts to reduce 4,4,6,6-tetramethylcyclohexenone, di-tert-butyl ketone, and benzophenone also failed to give esr signals even though these ketones are readily reduced by other methods.[1,9]

Reduction by basic DMSO solutions appears to require an unsaturated system to which the methylsulfinylcarbanion $(CH_3SOCH_2^-)$ can add readily. Thus, nitro aromatic and polynuclear aromatics are both reduced to their corresponding radical anions and methylated by the methylsulfinylcarbanion[10] and cyclooctatetraene is reduced to its radical ion.

---

†Experiment performed by Dr. Robert B. Brainard.

Acknowledgments: This work was supported by a Fellowship from Gulf Oil Co. to Ronald L. Blankespoor and by a grant from the National Institutes of Health.

References

(1) G. A. Russell and G. R. Stevenson, *J. Amer. Chem. Soc.*, **93**, 2432 (1971).

(2) O. L. Chapman and C. L. McIntosh, *J. Chem. Soc. D*, 770 (1971).

(3) C. H. DePuy, M. Isaks, K. L. Eilers, and G. R. Morris, *J. Org. Chem.*, **29**, 3503 (1964).

(4) E. W. Garbisch, Jr., *J. Org. Chem.*, **30**, 2109 (1965).

(5) A. D. McLachlan, *Mol. Phys.*, **3**, 223 (1960).

(6) W. Treibs and W. Schroth, *Justus Liebigs, Ann. Chem.*, **639**, 204 (1961).

(7) Y. Ikegami and S. Seto, *Bull. Chem. Soc. Jap.*, **41**, 2225 (1968).

(8) S. F. Nelsen and E. D. Seppanen, *J. Amer. Chem. Soc.*, **92**, 6212 (1970).

(9) G. A. Russell, D. F. Lawson, H. L. Malkus and P. R. Whittle, *J. Chem. Phys.*, **54**, 2164 (1971).

(10) G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).

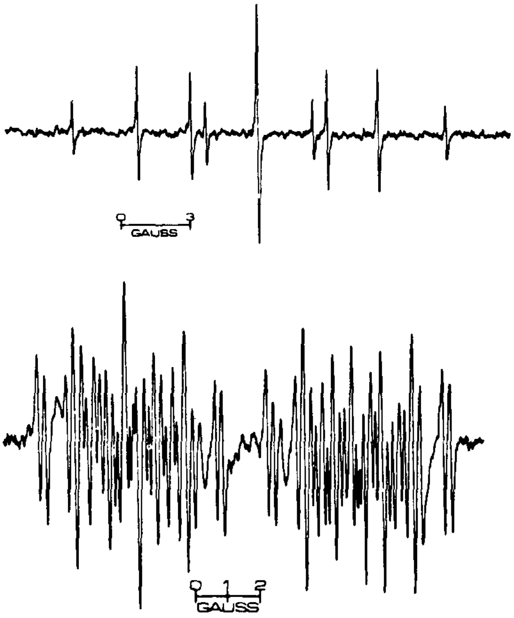


Figure. The first derivative esr spectra of (Ia·⁻) (top) and (II·⁻) (bottom) in DMSO at 30°.