vorotatory impurity which we have succeeded in separating (but not identifying) by preparative VPC.
(30) H. Gerlach and B. Zagalak, *J. Chem. Soc., Chem. Commun.*, 274 (1973).
(31) The unusually large specific rotations of tertiary amines **9**, **10**, and **11** are unprecedented among saturated chiral deuterium compounds,[32] but can be rationalized based upon unequal populations of conformations having opposite sign rotatory powers.[33]
(32) (a) L. Verbit, *Prog. Phys. Org. Chem.*, **7**, 51 (1970); (b) D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969); (c) B. Stephenson, G. Solladié, and H. S. Mosher, *J. Am. Chem. Soc.*, **94**, 4184 (1972); (d) P. H. Anderson, B. Stephenson, and H. S. Mosher, *ibid.*, **96**, 3171 (1974); (e) W. Meister, R. D. Guthrie, J. L. Maxwell, D. A. Jaeger, and D. J. Cram, *ibid.*, **91**, 4452 (1969).
(33) A. Moscowitz, D. A. Dixon, and L. Laux, University of Minnesota, private communication.
(34) Optically active allylic amines *E*-**14** and *Z*-**14** are assumed to be *R* and *S*, respectively, for reasons developed in the text.
(35) Exclusive formation of one geometric isomer in the reaction of α-methylallyl chloride with dimethylamine was noted by Young and Wilk.[20c]
(36) T. Oritani and K. H. Overton, *J. Chem. Soc., Chem. Commun.*, 454 (1978).
(37) C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, Ithaca, N.Y., 1969, pp 853-861.
(38) (a) A. Fry, *Pure Appl. Chem.*, **8**, 409 (1964); (b) D. C. Dittmer and A. F. Marcantonio, *Chem. Ind. (London)*, 1237 (1960); (c) *J. Am. Chem. Soc.*, **86**, 5621 (1964).
(39) H. C. Brown, "Organic Syntheses via Boranes", Wiley-Interscience, New York, 1975, p 258.
(40) J. Kenyon and D. R. Snellgrove, *J. Chem. Soc.*, 1169 (1925).
(41) W. F. Edgell and L. Parts, *J. Am. Chem. Soc.*, **77**, 4899 (1955).
(42) S. H. Pine and B. L. Sanchez, *J. Org. Chem.*, **36**, 829 (1971).
(43) R. S. Dewey and E. E. van Tamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961).

Ketyls of Cyclic α,β-Unsaturated Ketones. 2. Formation of Radical Anions by Electron Transfer Using Trimethylsilylsodium or Dimethyl Sulfoxide–Potassium *tert*-Butoxide[1]

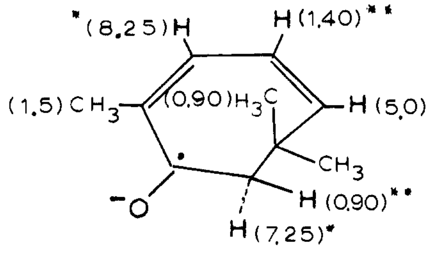
Glen A. Russell,* V. Malatesta, T. Morita, C. Osuch,[2] R. L. Blankespoor, Kathleen D. Trahanovsky, and E. Goettert

Contribution from the Department of Chemistry, Iowa State University, Ames, Iowa 50011. *Received October 15, 1978*

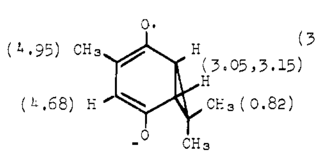
Abstract: Trimethylsilylsodium in HMPA readily reduces eucarvone, 4-substituted 2,5-cyclohexadienones, *N*-methyl-2-pyridone, maleic anhydride, phthalic anhydride, *N*-methylphthalimide, pyromellitic diimide, or *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione to the corresponding radical anions in a flow system wherein the radical anion can be detected within 0.1 s after mixing. Potassium *tert*-butoxide in Me_2SO gives only 1,4- and 1,2-semidiones from eucarvone in a flow system. Potassium *tert*-butoxide in Me_2SO converts diphenylcyclopropenone to diphenylcyclobutene-1,2-semidione, 3,7-cyclooctadiene-1,2-dione to a 5-substituted 3,6-cycloheptadiene-1,2-semidione, and cycloheptatriene to a 3-substituted tropone ketyl.

Ketyls have been detected from α,β-unsaturated ketones reduced electrolytically (DMF),[3] or by alkali metals in liquid ammonia.[4] In the present work we have treated a series of α,β-unsaturated carbonyl compounds statically or in a flow system with trimethylsilylsodium in HMPA,[5] or by potassium *tert*-butoxide in Me_2SO.[6]

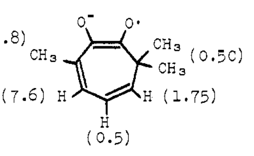
α,β-Unsaturated ketones containing enolizable hydrogen atoms α to either the carbonyl or the double bond form highly unstable ketyl radical anions, which can be detected by ESR spectroscopy in solution only under special conditions (e.g., flow experiments with alkali metals in liquid ammonia).[4] Flow experiments with trimethylsilylsodium in HMPA at 25 °C with 2-cyclohexenone or 2-cyclopentenone failed to produce any appreciable ESR signal. The only α,β-unsaturated ketone with an α-hydrogen atom that we have been able to convert to the ketyl radical anion in this system has been eucarvone. Mixing eucarvone in HMPA and trimethylsilylsodium in HMPA under argon gave a well-resolved ESR signal in a flow system 90 ms after mixing (Figure S1a). Under stopped flow the spectrum of **1** disappeared immediately. The ketyl (**1**) is not a planar molecule as evidenced by the magnetic nonequivalence of the α-hydrogen atoms. The carbonyl groups and the four vinyl carbons can form a coplanar arrangement with one hydrogen atom of the α-methylene group and one methyl group of the *gem*-dimethyl in an equatorial position. This leads to the assignment of hfsc as shown.[7] It has been previously recognized that carbon atoms of conjugated vinyl groups β or δ to the ketyl or semidione spin labels carry considerable spin density.[3,4,8]



1, a^H in gauss
*, **, hfsc could be reversed



2, a^H in gauss



3, a^H in gauss

As a test of the relative reducing ability of the system potassium *tert*-butoxide in Me_2SO, eucarvone was subjected to flow and stopped-flow experiments. Ketyl **1** was never observed. Instead, oxidation products **2** (Figure S1b) and **3** (Figure S1c) were detected even with carefully deoxygenated solutions. Potassium *tert*-butoxide in Me_2SO is not only a poorer reducing agent than trimethylsilylsodium in HMPA, but it is more apt to give oxidation products from traces of oxygen remaining in the solution. At flow rates between 0.1 and 20 s between mixing and detection the previously described bicyclic 1,4-semidione **2**[9] was observed. Under stopped flow **2** decayed and the spectrum of **3** could be detected for ap-

0002-7863/79/1501-2112$01.00/0

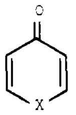
Table I. Hyperfine Splitting Constants in Gauss for **4a–e**$^{-}\cdot$, 25 °C

ketyl	solvent	a_{α}^{H}	a_{β}^{H}	other
4a	HMPA	1.00	6.75	
4a	Me_2SO	1.13	7.00	
4a	DMF[a]	1.14	7.05	
4b	HMPA	1.6	7.55	line width 0.7 G
4c	DMF	0.27	5.5	$a_{CH_3}^{H}$ = 0.27 (6 H)
4d	HMPA	3.2		$a_{CH_3}^{H}$ = 3.2 (6 H)
4e	DMF	0.61	5.2	

[a] Reference 3.

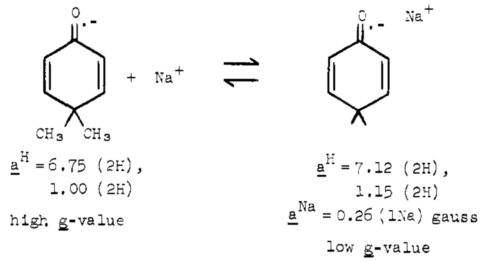
proximately 1 h, after which more complex ESR signals were observed. Semidione **3** is a planar molecule, at least on a time average, as indicated by the magnetic equivalence of the *gem*-dimethyl group. The high spin density observed at the β-carbon atom is consistent with other studies of conjugated unsaturated 1,2-semidiones.[8]

We have examined a series of 2,5-cyclohexadienones, **4a–e.**



4a, X = $C(CH_3)_2$
4b, X = $C(C_6H_5)_2$
4c, X = $Si(CH_3)_2$
4d, X = O;3,5-dimethyl
4e, X = S

Semidione **4a**$^{-}\cdot$ was formed in a high concentration in the trimethylsilylsodium system. The ESR signal is easily detected at slow flow rates approximately 1–2 s after mixing (3 mL/min flow through a 0.05-mL cell). At high concentrations of trimethylsilylsodium only the ion pair could be detected (hfs by a single Na^+), Figure S2a. However, at lower sodium ion concentrations a mixture of the free ketyl and ion pair could be seen simultaneously (Figure S2b) with no indication of exchange ($\tau > 10^{-5}$ s), Δg = 0.000 17.

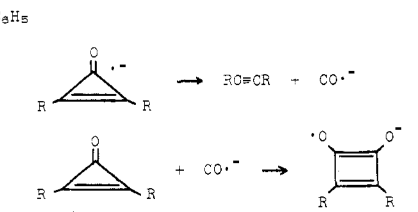


The relationship between *g* value, a^H, and structure parallels previous observations on semidione radical anions and ion pairs (i.e., the ion pairs always possess low *g* values and higher values of a^H than the free ions).[10] Semidione **4a**$^{-}\cdot$ can also be seen in flow experiments with potassium *tert*-butoxide in Me_2SO. A weak signal (a^H = 7.00 (2 H), 1.13 (2 H)) can be seen 1 s after mixing and a fairly strong signal with 0.1 s between mixing and detection.

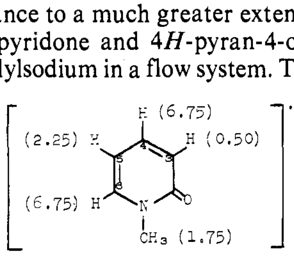
Ketyls **4b**$^{-}\cdot$ and **4d**$^{-}\cdot$ were observed in the trimethylsilylsodium-HMPA system under slow flow (1 s) and fast flow (0.1 s), respectively. Ketones **4c** and **4e** were not available in sufficient quantities for flow experiments, and the ketyls were prepared by electrolytic reduction in DMF containing tetrabutylammonium perchlorate. The observed hfsc values are summarized in Table I.

The values of a^H for the α and β positions are quite similar for **4c** and **4e** (X = $>Si(CH_3)_2$, > S). Both substituents have an appreciable effect on the spin distribution when compared to **4a**$^{-}\cdot$ (X = $>C(CH_3)_2$).[11] Substitution of an oxygen atom at the 4 position (**4d**$^{-}\cdot$) has an appreciably greater effect on spin distribution. The oxygen atom is apparently involved in aromatic resonance to a much greater extent than sulfur.

Scheme I



N-Methyl-2-pyridone and 4*H*-pyran-4-one were treated with trimethylsilylsodium in a flow system. The pyridone gave



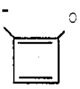
5

a^H in gauss, a^N = 3.5 gauss

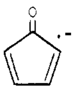
quite a stable radical anion, but no ketyl could be detected from 4*H*-pyran-4-one. Neither system gave a detectable radical anion with basic Me_2SO. The hfsc values were assigned for **5** on the basis of Hückel, McLachlan, and INDO calculations using the known geometry of the parent molecule[12] (Table SII). The spin density at C-4 and C-6 was considerably greater than at C-3 or C-5 in all of the calculations.

The cyclically conjugated series of ketyls and semidiones (**6–11**) are of interest. At present only **7–10** are known.[13]

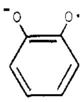
6



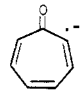
7



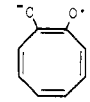
8



9



10

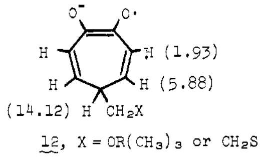


11

Ketyls **8** and **10** are readily prepared by reduction of the ketones with potassium *tert*-butoxide in Me_2SO,[6] or in the case of **10** by trimethylsilylsodium in HMPA.[13]

Reaction of diphenylcyclopropenone with potassium *tert*-butoxide in Me_2SO gave surprising results. At first flow of 1-3 s between mixing and detection an unknown radical (obviously not **6**) could be detected (Figure S3a) which appeared to be a triplet of triplets ($a^H \sim$ 1.55, 0.50 G). However, the intensities deviated badly from 1:2:1 triplets. Probably the spectrum is a result of two pairs of not quite equivalent hydrogen atoms. Upon stopped flow this spectrum disappeared and was replaced by an excellently resolved spectrum of **7**[14] (Figure S3b) whose persistency is similar to that of *o*-benzosemiquinone (**9**). A carbonyl insertion reaction has occurred. Presumably this process follows the general outline of Scheme I, which has been documented in several other cases with strained-ring ketones.[15-17]

One possible route to **11** involves the conversion of 3,7-cyclooctadiene-1,2-dione[18] to the dianion, which in the presence of traces of oxygen might form **11** or one of its valence isomers.[19] Treatment of the octadienedione in Me_2SO with potassium *tert*-butoxide in a flow system produced an ESR signal of a radical ion with sufficient stability for detection for a few minutes in a static system. The spectrum (Figure S4), however, is not consistent with structure **11,** but the hfsc values (a^H = 14.12 (1 H), 5.88 (2 H), 1.93 (2 H) G) are suggestive of a 5-substituted 1,2-cycloheptatriene-1,2-semidione, e.g., **12.**[10]



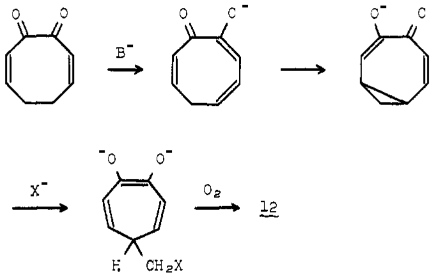
12, X = $OR(CH_3)_3$ or CH_2SOCH_3

Table III. Hfsc Values of Cyclically Conjugated Ketyls and Semidiones (Me_2SO, K^+, 25 °C)

	H-2	H-3	H-4	H-5	H-6	H-7	other
3-phenyl-**7**[a]	6.4						1.83 (1 H), 1.60 (2 H), 0.55 (2 H)
3,4-diphenyl-**7**							1.30 (2 H), 1.20 (4 H), 0.48 (4 H)
8[b]	2.9	5.3	5.3	2.9			
9		1.16	3.65	3.65	1.16		
10[b]	8.6	0.10	5.1	5.1	0.1	8.6	
11 (HMPA)	8.56	0.175	5.00	5.00	0.178	8.56	

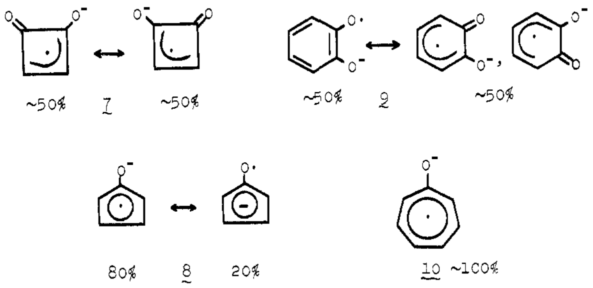
[a] Reference 14. [b] Reference 13.

Scheme II



The formation of **12** from the initial monoenolate anion can be easily rationalized as in Scheme II. Reaction of 2,7-cyclooctadienone with lithium diisopropylamide followed by benzoyl peroxide yielded a keto benzoate. However, from the ^1H NMR it was not obvious whether this was a 1,2- or a 1,4-keto benzoate. Treatment of this keto benzoate with potassium *tert*-butoxide in Me_2SO also formed **12**, and this proves that the keto benzoate is 2-benzoyloxy-3,7-octadienone (**13**) (Scheme III). In a similar fashion 2,7-cyclooctadienone reacted with lead tetraacetate to give a keto acetate which in basic Me_2SO formed **12**. Treatment of 1-trimethylsiloxycycloocta-1,3,7-triene with *m*-chloroperbenzoic acid formed a hydroxy ketone which also gave **12** upon treatment with potassium *tert*-butoxide in Me_2SO.

The spin distributions in **7–10** shown in Table III are interesting. If for **7–10** the spin density at the carbonyl carbon atoms is assumed to be equal to the spin density at the alternate atom C-3 (or the average of spin densities when two different alternate atoms are present), the following spin densities ($\Sigma\rho_C$) are calculated for the carboxyclic ring systems ($|Q_{CH}{}^H| = 27$): C_4 (**7**), $\Sigma\rho_C = 0.92$; C_5 (**8**), $\Sigma\rho_C = 0.80$; C_6 (**9**), $\Sigma\rho_C = 0.53$; C_7 (**10**), $\Sigma\rho_C = 1.0$ ($\rho_C{}^{1,3,6}$ are negative). These spin densities emphasize that the important resonance contributions vary considerably between **7** and **9** and between **8** and **10** as shown below.



Scheme III

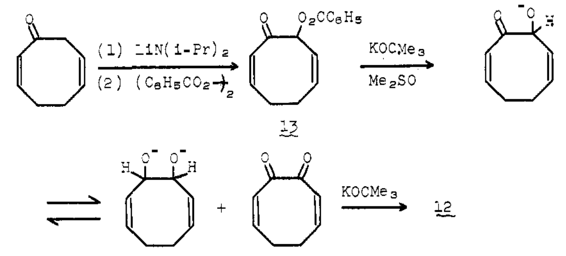
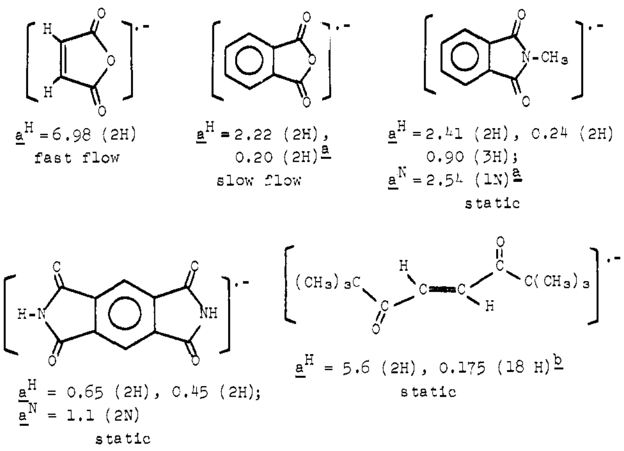


Chart I. Hyperfine Splitting Constants in Gauss



$a^H = 6.98$ (2H) fast flow

$a^H = 2.22$ (2H), 0.20 (2H)[a] slow flow

$a^H = 2.41$ (2H), 0.24 (2H) 0.90 (3H); $a^N = 2.54$ (1N)[a] static

$a^H = 0.65$ (2H), 0.45 (2H); $a^N = 1.1$ (2N) static

$a^H = 5.6$ (2H), 0.175 (18 H)[b] static

[a] Reference 21. [b] Reference 22.

Potassium *tert*-butoxide in Me_2SO has been employed in a flow system to reduce maleic anhydride to the corresponding radical anion, but this system will not reduce phthalic anhydride.[6] Trimethylsilylsodium in HMPA is much more effective for the reduction of these and other 1,4-dicarbonyl compounds. Chart I lists a series of radical anions observed in flow or static systems using trimethylsilylsodium.

The mechanism of the reduction by trimethylsilylsodium–HMPA and potassium *tert*-butoxide in Me_2SO may differ considerably. In the first case apparently a direct electron transfer occurs with the possible intervention of π or σ complexes in certain cases.[23] We do not believe that in the Me_2SO system either the *tert*-butoxide or methylsulfinylmethide anion ($CH_3SOCH_2^-$) is effective in one electron transfer. Instead we believe that the methylsulfinylmethide anion can add to certain π systems to generate a delocalized anion (or dianion after loss of a proton), which can now transfer an electron to a second π molecule (Scheme IV). The reducing ability of basic Me_2SO systems therefore depends upon the ease of formation of the initial σ adduct ($CH_3SOCH_2\pi^-$). Thus, potassium *tert*-butoxide in Me_2SO will reduce maleic anhydride but not phthalic anhydride; benzil but not benzophenone; anthracene but not biphenyl, stilbene, or tolane. In the case of the anthracene, basic Me_2SO yields methylated anthracenes and radical anions derived from them can be seen as the reaction progresses.[24]

Both trimethylsilylsodium and basic Me_2SO reduce cyclooctatetraene to the radical anion. Neither forms the cycloheptatriene radical anion from cycloheptatriene, but the reaction with $CH_3SOCH_2^-$ gives an interesting paramagnetic product (Figure 5), which illustrates the side reactions which can occur when the dimsylate anion is used as the reductant.

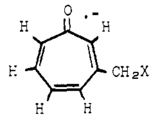
Scheme IV

$$\mathrm{CH_3SOCH_2:^-} + \pi\text{-H} \longrightarrow \mathrm{CH_3SOCH_2}\text{-}\pi\text{-H}^{-1} \overset{-\mathrm{H}^+}{\rightleftharpoons} \mathrm{CH_3SOCH_2}\text{-}\pi^{-2}$$

$$\mathrm{CH_3SOCH_2}\pi^{-2} + \pi \longrightarrow \pi^{\cdot -} + \mathrm{CH_3SOCH_2}\pi^{\cdot -}$$

$$\mathrm{CH_3SOCH_2}\pi^{\cdot -} + \pi \rightleftharpoons \pi^{\cdot -} + \mathrm{CH_3SOCH_2}\pi$$

The radical shown in Figure 5 is the only species detected in a flow experiment where cycloheptatriene and potassium *tert*-butoxide in Me_2SO are mixed. A trace of oxygen is required to produce the spectrum. The radical anion is stable for up to 30 min under stopped-flow conditions, and several minutes are required after mixing for the species to be formed in detectable amounts. The rich hyperfine structure of narrow lines with values of a^H = 8.2 (1 H), 7.8 (1 H), 5.2 (1 H), 4.6 (1 H), and 0.3 (2 H) is very suggestive of a 3-substituted tropone ketyl, **14.** Ketyl **14** could be formed by the addition of the dimsylate anion to cycloheptatriene followed by a series of oxygenation and dehydrogenation reactions (Scheme Va). A more intriguing possibility is that the dimsylate anion undergoes a [4 + 6] cycloaddition reaction to give an unstable intermediate which undergoes ring opening and oxidative dehydrogenation to yield **14** (Scheme Vb). The regioselectivity observed seems most consistent with process (b).



14, $X = CH_3S^-$ or CH_3SO^-

Experimental Section

ESR spectra were recorded with a Varian E-3 or V-4502 spectrometer. Flow experiments used a Varian Associates V-4549A flow cell (~0.05 mL between the point of mixing and detection). HMPA solutions under argon were mixed under gravity flow, while most Me_2SO flow experiments used 50-mL polyethylene syringes driven by a Harvard Apparatus Co. compact infusion pump. The syringes were loaded in a nitrogen drybox, and the solutions were deaerated by prepurified nitrogen for approximately 30 min before the syringes were sealed. Polyethylene tubing was used in both sets of flow experiments.

The Me_2SO and HMPA employed were freshly distilled under vacuum and stored over molecular sieves. In some cases the HMPA was distilled from sodium. Flow experiments in Me_2SO typically mixed equal volumes of the substrate at 0.1 M and potassium *tert*-butoxide at 0.3 M concentrations. The HMPA experiments typically involved mixing equal volumes of the substrate in HMPA (0.05 M) and trimethylsilylsodium (0.05 M) prepared by reaction of sodium methoxide with hexamethyldisilane in purified HMPA under argon.

Commercial samples (Aldrich Chemical Co.) of 3,5-dimethyl-4-pyran, 4*H*-pyran-4-one, *N*-methyl-2-pyridone, diphenylcyclopropenone, tropone, maleic anhydride, phthalic anhydride, *N*-methylphthalimide, and pyromellitic diimide were used. The syntheses of the eucarvone,[21] 4,4-dimethyl-2,5-cyclohexadienone,[3] and *trans*-2,2,7,7-tetramethyl-4-octene-3,6-dione[22] have been described. Cycloheptatriene (Shell or Aldrich) was rectified in a Todd column (bp 114–115 °C) and purified by GC using an ODPN column at 80 °C and an SF-96 column at 90 °C. Commercial cycloheptatriene gave the same ESR result as a sample prepared by the reaction of sodium borohydride with tropylium tetrafluoroborate. Synthetic Me_2SO (from trimethylsulfoxium iodide)[26] was also employed in the formation of the radical anion from cycloheptatriene.

4,4-Dimethyl-4-sila-2,5-cyclohexadienone was prepared by dehydrogenation of 4,4-dimethyl-4-silacyclohexanone by dicyanodichloroquinone.[27] 4-Thia-2,5-cyclohexadien-4-one (mp 107–108 °C, lit.[28] mp 110 °C) was prepared from 4-thiacyclohexanone[29] by the literature method.[28]

3,7-Cyclooctadienedione was prepared from 2,6-cyclooctadienone by the method of Oda.[19] Reaction of 2,6-cyclooctadienone,[30] bp 45–48 °C (0.8 Torr), lit.[29] bp 42–44 °C (0.4 Torr), with 1.1 equiv of lead tetraacetate in refluxing benzene for 6 days gave, after washing with water, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl solutions followed by drying with $MgSO_4$ and removal of the solvent under vacuum, a mixture of the starting ketone and **2-acetoxy-3,7-cyclooctadienone.** Chromatography on silica gel gave the pure acetoxy ketone (by GC and TLC) upon elution with hexane (90%)-ethyl acetate (10%): IR (neat) 1750, 1690, 1665, 1648, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1 (s, 3), 1.7–3.2 (m, 7), 5.3–6.6 (m, 5); high-resolution mass spectrum 180.796 (calcd for $C_{10}H_{12}O_3$, 180.0786). The final structure proof for this keto acetate is its conversion into the 1,2-semidione **12. 2-Benzoyloxy-3,7-cyclooctadienone** was prepared by treatment of 4 mmol of 2,7-cyclooctadienone with 4 mmol of lithium diisopropylamide in THF at −78 °C. After 10 min at −78 °C 4 mmol of benzoyl peroxide was added. The solution was stirred for 15 min at −78 °C and allowed to warm to room temperature. The reaction was quenched with water and the mixture extracted with methylene chloride. The methylene chloride solution was dried ($MgSO_4$), the solvent evaporated, and the resulting oil chromatographed on Florisil to give the benzoyloxy ketone as a yellow oil in 30% yield. **1-Trimethylsiloxy-1,3,7-cyclooctatriene** was prepared from a mixture of 2.7 mmol of cycloocta-2,6-dienone and 2.7 mmol of lithium diisopropylamide, which was treated with 2.7 mmol of trimethylchlorosilane after 15 min at −78 °C. The mixture was stirred for 10 min at −78 °C and allowed to warm to room temperature. Addition of water followed by ether extraction and filtration through dry silica gel (ether (20%)-pentane (80%) solvent) gave 2.6 g of the siloxy derivative: ^1H NMR ($CDCl_3$) δ 0.2 (9 H), 2.3 (m, 4), 5.2–5.8 (m, 5). **2-Hydroxycycloocta-3,7-dieneone** was prepared from the reaction of 1-trimethylsiloxy-1,3,7-cyclooctatriene (1.6 mmol) in 10 mL of methylene chloride with 4 mL of 0.5 M aqueous $NaHCO_3$ and 1.4 mmol of *m*-chloroperbenzoic acid. After 30 min the organic layer was separated and extracted with aqueous $NaHCO_3$ and saturated aqueous NaCl. Evaporation of the solvent gave 190 mg (65%) of the hydroxy ketone identified on the basis of the ESR spectrum in potassium *tert*-butoxide–Me_2SO.

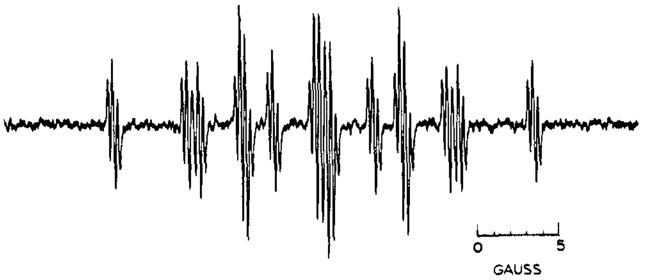
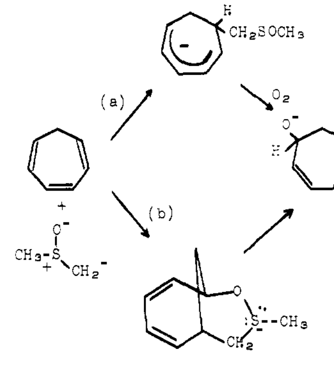


Figure 5. Paramagnetic reaction product observed in the reaction of cyclohexatriene, potassium *tert*-butoxide, and Me_2SO in the presence of a trace of air.

Scheme V

X = CH_3SO- in (a), CH_3S- in (b)



Supplementary Material Available: Table SII, observed and calculated hfsc values for *N*-methyl-2-pyridone radical anion; Figures S1-S4, the ESR spectra for paramagnetic products observed from eucarvone, 4,4-dimethylcyclohexadienone, diphenylcyclopropenone, and 3,7-cyclooctadiene-1,2-dione (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Electron Transfer Processes. 17. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.
(2) National Science Foundation Predoctoral Fellow, 1976–1978.
(3) G. A. Russell and G. R. Stevenson, *J. Am. Chem. Soc.*, **93**, 2432 (1971).
(4) I. H. Elson, T. J. Kemp, and T. J. Stone, *J. Am. Chem. Soc.*, **93**, 7091 (1971).
(5) H. Sakurai, A. Okada, M. Kira, and K. Yonezawa, *Tetrahedron Lett.*, 1511 (1971); H. Sakurai and A. Okada, *J. Organomet. Chem.*, **35**, C13 (1972); H. Sakurai, A. Okada, H. Umine, and M. Kira, *J. Am. Chem. Soc.*, **95**, 955 (1973).
(6) G. A. Russell and R. L. Blankespoor, *Tetrahedron Lett.*, 4573 (1971).
(7) Similarly, 5,5-dimethyl-2-cyclohexenone ketyl[4] is nonplanar with a_3^H = 13, a_2^H = 0.72, a_6^H = 12.9, 4.35 G.
(8) G. A. Russell, R. L. Blankespoor, K. D. Trahanovsky, C. S. C. Chung, P. R. Whittle, J. Mattox, C. L. Myers, R. Penny, T. Ku, Y. Kosugi, and R. S. Givens, *J. Am. Chem. Soc.*, **97**, 1906 (1975).
(9) G. A. Russell, T. Ku, and G. Lokensgard, *J. Am. Chem. Soc.*, **92**, 3833 (1970); G. A. Russell, J. R. Dodd, T. Ku, C. Tanger, and C. S. C. Chung, *ibid.*, **96**, 7255 (1974).
(10) G. A. Russell and C. E. Osuch, *J. Am. Chem. Soc.*, **100**, 5979 (1978).
(11) See J. A. Redford, J. R. Bolton, A. Carrington, and R. H. Prince, *Trans. Faraday Soc.*, **59**, 53 (1963).
(12) B. R. Penfold, *Acta Crystallogr.*, **6**, 591 (1953).
(13) Diphenylcyclopropenone ketyl has been observed at −60 °C in DMF with a half-life of ~20 min. Under these conditions, the ketyl decarbonylates to the radical anion of diphenylacetylene (P. Fürderer, F. Gerson, and A. Krebs, *Helv. Chim. Acta*, **60**, 1226 (1977)). Excellent precursors to **8** and **10** are the corresponding hydroperoxides which yield the ketones in situ when treated with basic Me_2SO (G. A. Russell, T. Takano, and Y. Kosugi, *J. Am. Chem. Soc.*, **101**, 1491 (1979)).
(14) G. A. Russell, V. Malatesta, and R. L. Blankespoor, *J. Org. Chem.*, **43**, 1837 (1978).
(15) G. A. Russell, V. Malatesta, D. E. Lawson, and R. Steg, *J. Org. Chem.*, **43**, 2242 (1978).
(16) G. A. Russell, D. F. Lawson, and L. A. Ochrymowycz, *Tetrahedron*, **26**, 4697 (1970); G. A. Russell, D. F. Lawson, H. L. Malkus, and P. R. Whittle, *J. Chem. Phys.*, **54**, 2164 (1971).
(17) J. P. Dirlam and S. Winstein, *J. Org. Chem.*, **36**, 1559 (1971).
(18) Y. Kitahara, M. Oda, and S. Miyakosi, *Tetrahedron Lett.*, 4141 (1975).
(19) G. A. Russell, K. Schmitt, C. Tanger, E. Goettert, M. Yamashita, Y. Kosugi, J. Siddens, and G. Senatore, "Organic Free Radicals", American Chemical Society Symposium Series 69, W. A. Pryor, Ed., 1978, pp 376–399.
(20) The large value of a_5^H results from the coefficients in the HOMO at C-4 and C-6 having the same sign since $a_5^H = f(c_4 + c_6)^2$: D. H. Whiffen, *Mol. Phys.*, **6**, 224 (1963); G. A. Russell and P. R. Whittle, *J. Am. Chem. Soc.*, **89**, 4781 (1967).
(21) These radical anions have also been prepared by electrolytic reduction in Me_2SO: S. F. Nelsen, *J. Am. Chem. Soc.*, **89**, 5257 (1967).
(22) Also prepared by electrolysis: G. A. Russell, R. L. Blankespoor, J. Mattox, P. R. Whittle, D. Symalla, and J. R. Dodd, *J. Am. Chem. Soc.*, **96**, 7249 (1974).
(23) G. A. Russell, E. G. Janzen, and E. T. Strom, *J. Am. Chem. Soc.*, **86**, 1807 (1964).
(24) G. A. Russell and S. A. Weiner, *J. Org. Chem.*, **31**, 248 (1966).
(25) G. A. Russell, "Techniques of Chemistry", Vol. IV, Part 1, A. Weissberger, Ed., Wiley, New York, 1972, p 449.
(26) F. A. Cotton, J. H. Fassnacht, W. D. Horrocks, Jr., and N. A. Nelson, *J. Chem. Soc.*, 4138 (1959).
(27) R. A. Felix and W. P. Weber, *J. Org. Chem.*, **37**, 2323 (1972).
(28) F. Arndt and N. Bekir, *Chem. Ber.*, 2393 (1930).
(29) P. Y. Johnson and G. A. Berchtold, *J. Org. Chem.*, **35**, 584 (1971).
(30) T. S. Cantrell and J. J. Solomon, *J. Am. Chem. Soc.*, **92**, 4656 (1970).

Regiocontrolled Anodic Cyanation of Nitrogen Heterocycles. Pyrroles and Indoles

Kunihisa Yoshida

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan.

Received May 25, 1978

Abstract: A series of 1-substituted pyrroles and indoles was potentiostatically oxidized at platinum sheet. The anolyte was methanol–sodium cyanide and the reference electrode an SCE. In all instances substitution with cyanide ion was achieved. Annular replacement at a free 2 (or 5) position was favored for pyrroles lacking the substituent on either 2 or 5 (or both) position(s), whereas lateral substitution was favored for compounds with the methyl group on both 2 and 5 positions. Methyl displacement by the cyano group occurred slightly in some cases. The methyl or phenyl group at the 1 position was not attacked. Cyanation of indoles occurred exclusively on the pyrrole moiety of the molecule. In this case side-chain substitution was not observed. A scheme involving initial electron loss from the organic substrates, followed by a fast chemical reaction, can well elucidate products, coulometric data, and voltammetric results. A comparison with the photosensitized electron transfer cyanation in the same solvent system indicates that the above anodic system involves initial cation radical formation. Pyrrolecarbonitriles, annular substitution products, come from direct nucleophilic attack by cyanide ion on methylpyrrole cation radicals prior to competitive deprotonation from a methyl substituent. An MO calculation for the cation radicals by the ω technique supports the observed positional reactivity.

Introduction

The oxidation potential of cyanide ion is considerably low compared with common organic compounds,[1] so cyanide ion in homogeneous solution will not survive the potential necessary to oxidize the reactant. Indeed, there are apparently no reports in the literature describing chemical cyanations that are analogous to the electrochemical reaction.[2]

The discharge of cyanide ion in aqueous solution at a platinum electrode proceeds through an initial irreversible one-electron oxidation with $E_{1/2} \simeq 0.6$ V vs. SCE,[4] while chronopotentiometry in acetonitrile reveals a poorly defined, elongated oxidation transition with $E_{1/4} \simeq 0.9$ V vs. Ag^+/Ag.[5] Potentiostatic steady-state measurements[6,7] and cyclic voltammetry for the $NaCN/CH_3OH$ system indicate no substantial oxidation up to 1.6 V vs. SCE. It is the large positive shift in the anodic limit for this solvent system which permits the electrochemical method to work successfully.

In the last few years[8] we made attempts to avoid a concurrent methoxylation and eventually found this method to be quite useful for the cyanation of compounds containing nitrogen atom(s) or extended π-electron systems.

The present paper describes an anodic cyanation of nitrogen heterocycles.[9] 1-Methylpyrrole (**1**) can, for example, be converted to 1-methylpyrrole-2-carbonitrile (**11**), which can subsequently undergo anodic oxidation to afford 1-methylpyrrole-2,5-dicarbonitrile. Equations 1 and 2 are illustrative.

0002-7863/79/1501-2116$01.00/0