

appears to be formed in only a minor amount, if at all.^{3a} This preferential elimination of methyl carbanion from III must be caused by the following factors: (a) elimination of the most stable carbanion would be expected, hence the I^o methyl carbanion in preference to the II^o C-9 carbanion; and (b) elimination of methyl carbanion involves a favored diaxial *trans* elimination with the electron pair at C-1 (or C-5) displacing the angular methyl group.⁴

(3a) NOTE ADDED IN PROOF.—Although to date we have neither isolated IV from our reaction nor been able to establish that it is formed in even a minor amount, we have just learned from Dr. R. M. Dodson that he has prepared IV by an unequivocal method. We are indebted to Dr. Dodson for informing us of his results prior to publication and for sending us a sample of IV.

(4) Although our reaction bears an apparent resemblance to the zinc dust-pyridine aromatization of certain steroidal dienones and trienones reported recently by K. Tsuda, E. Ohki, and S. Nozoe [*J. Org. Chem.*, **28**, 783 (1963)], the two reactions must be very different mechanistically. The zinc dust-pyridine aromatization of Ia is reported to give only a 4% yield of estrone; the major product (80%) is 4-methylestra-1,3,5(10)-trien-1-ol-17-one resulting from dienone-phenol rearrangement.

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Molybdate- and Tungstate-Catalyzed Fixation of Nitrogen

Sir:

The apparent correspondence between the catalysis by molybdates of the reduction of nitrate in acidic solution¹ and the molybdenum requirement of nitrate reductase² in biochemical systems led us to consider whether or not molybdate would catalyze the reduction of molecular nitrogen in aqueous acid. Molybdate is a requirement of nitrogen-fixing legumes which suggests that it might catalyze nitrogen fixation in inorganic systems.

We have attempted cathodic reduction using platinum electrodes and porous graphite electrodes through which nitrogen was bubbled and by bubbling nitrogen

TABLE I

Reducing agent	Catalyst ^a	Medium	NH ₄ ⁺ formed, moles/l.
Pt cathode	MoO ₄ ⁻²	3 M HCl	~10 ^{-4b}
Porous graphite cathode (PGC)	MoO ₄ ⁻²	3 M HCl	10 ⁻⁴ -10 ^{-3b}
PGC	MoO ₄ ⁻²	Phosphate buffer, pH 7	~10 ^{-4b}
PGC	MoO ₄ ⁻² + catechol	Phosphate buffer, pH 7	<10 ⁻⁶
Zn metal	MoO ₄ ^{-2c}	3 M HCl	~10 ⁻⁴
SnCl ₂	WO ₄ ^{-2c}	12 M HCl	~10 ^{-3d}

^a Less than 10⁻⁶ M NH₄⁺ was obtained during all electrolyses done in the absence of catalyst for periods of 1-7 days. ^b NH₄⁺ production ceased when all Mo(VI) was reduced to Mo(III), usually during first 24 hr. ^c No experiments without catalyst were performed. ^d NH₄⁺ still increasing after 2 weeks.

through aqueous acids containing molybdic acid under conditions previously found favorable to the reduction of nitrate¹ and in phosphate buffers at pH 7.0. We have also bubbled nitrogen through solutions of tungstic acid containing stannous chloride in which perchlorate has been found to be reduced.³ In all cases, small concentrations of ammonium ion were found (10⁻⁴ to 10⁻³ M, or 10 to 100 times the detection limit using our sampling procedure). A Kjeldahl separation followed by a spectrophotometric test using Nessler's reagent was employed for detecting ammonium ion. No ammonium ion was found after electrolysis was performed in the absence of molybdenum, nor when molybdate was bound in a chelate complex with catechol [Mo(VI)-(catechol)₂] during the electrolysis.

All reagents were determined to be free of nitrate and ammonium ions. Nitrogen gas was scrubbed with 3 M hydrochloric acid and found free of ammonia. Great care was taken to prevent introduction of ammonia from any source other than reduction of nitrogen gas.

Successful electrolyses ceased to produce further ammonium ion during the first 24 hr., at which time the molybdenum was quantitatively reduced to Mo(III).

One experiment employing a zinc reductor gave positive results, but no control on the catalyst has been tried.

One experiment involving bubbling nitrogen through a stannous chloride and tungstic acid solution in concentrated hydrochloric acid gave continuously increasing concentrations of ammonium ion (~10⁻³ M) over a 2-week period. The ammonium ion must come from nitrogen, but whether tungstic acid is necessary is not yet known.

Some similarities to patterns of catalytic behavior of Mo(VI) and W(VI) toward reduction of oxy-ions is noted.^{1,3,4} Catalysis ceases if Mo(VI) is reduced to Mo(III) in reductions of perchlorate,⁴ nitrate,¹ and nitrogen. Tungsten(VI) is not reduced by Sn(II), thus it remains in a catalytically active higher state.³

Mo(IV) has been postulated to be much more catalytically active than Mo(V) or Mo(VI) at room temperature^{1,4} in reference to oxy-ion reduction. Since Mo(IV) and Mo(V) form stable complexes with CN⁻, which is isoelectronic with N₂, interaction of N₂ with Mo(IV) or Mo(V) to form activated complexes in which the N-N bond is weakened is a fair possibility.

Although the production of ammonium ion is small, the failure to produce it in the absence of catalyst and our fortuitous finding of a catalyst poison (catechol) lend credence to the results. It is certain that 10⁻⁴ M ammonium ion would represent a large concentration

(1) G. P. Haight, Jr. and A. Katz, *Acta Chem. Scand.*, **16**, 659 (1962).

(2) D. J. Nicholas, A. Nason, and W. D. McElroy, *J. Biol. Chem.*, **207**, 341 (1954).

(3) G. P. Haight, Jr., *J. Am. Chem. Soc.*, **76**, 4718 (1954).

(4) G. P. Haight, Jr., and W. F. Sager, *ibid.*, **74**, 6056 (1952).

for a legume with no other source of nitrogen. Table I summarizes experiments completed thus far.

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Formation of Alicyclic Semiquinones. Conformational Analysis by Electron Spin Resonance¹

Sir:

Paramagnetic intermediates in the basic oxidation of aromatic acyloins are recognized to be radical-anions of

electron by the aromatic rings. It was surprising to discover that base and traces of oxygen convert many alicyclic ketones (method 1) and α -ketols (method 2) to stable semiquinones. These radical-anions can also be prepared by electron transfer between 1,2-diketones and anions derived from acyloins^{2b} (method 3) or by electron transfer between 1,2-diketones and other carbanions, such as $[\text{C}_6\text{H}_5\text{COCHCH}_3]^-$ (method 4).

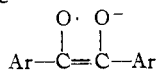
In a typical experiment, air-saturated solutions of a ketone (0.05 *M*) and potassium *t*-butoxide (0.1 *M*) in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) are mixed under nitrogen. In many cases an e.s.r. spectrum can be detected immediately. Use of too much oxygen gives rise to other stable radicals in addition to the desired semiquinones. Oxidation of the acyloins is best performed using partially deoxygenated

TABLE I
CONFORMATIONS OF CYCLOALKANEDIONE RADICAL-ANIONS

Radical-anion	Method of prepn.	$a_{\alpha\text{-H}}$ (gauss) ^a		$\theta_{\text{axial-H}}$	$B\rho$	ρ^b
		axial	equatorial			
Cyclopentane-1,2-dione	1	14.16 ^c		(+27) ^{c,d}	17.8	0.30
4- <i>t</i> -Butylcyclohexane-1,2-dione	1	13.10	6.55	+13	13.8	.24
Cyclohexane-1,2-dione	1, 2, 3, 4	9.82 ^c		(+43) ^c	13.8 ^e	.24
Cycloheptane-1,2-dione	1	6.70	1.97	+3 or -50	6.7 or 16.7	.11 or .29
Cyclooctane-1,2-dione	1	3.33 ^f		(+30 or -60) ^f	4.4 or 13.3	.08 or .23
Cyclononane-1,2-dione	1	12.57	5.49	+11	13.0	.22
Cyclodecane-1,2-dione	1, 2	8.33	~0	~-30	11.1	.19
Cyclododecane-1,2-dione	1	7.88	~0	~-30	10.5	.18
Cyclopentadecane-1,2-dione	1	7.23	2.07	+2 or -50	7.2 or 17.5	.12 or .30
Camphorquinone	1, 4	$a_{\text{methyl-H}} = 2.66^g$				
Tropane-1,2-dione	1	$a_{\text{methyl-H}} = 5.95$, $a_{\text{single-H}} = 1.90$				
1-Phenylpropane-1,2-dione	1	$a_{\text{methyl-H}} = 3.46$				
1-Phenylbutane-1,2-dione	1	$a_{\text{methylene-H}} = 3.42$				
<i>t</i> -Butylphenylglyoxal	2	$a_{\text{methyl-H}} = 0.17$				
Di- <i>t</i> -butylglyoxal	2	$a_{\text{methyl-H}} = 0.31^h$				

^a In dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%). ^b $B = 58.5$ gauss. ^c Four equivalent protons. ^d Radical-anion assumed planar and with geometry similar to cyclopentene (ref. 7). ^e Assumed equal to $B\rho$ for *t*-butyl compound. ^f Four nearly equivalent protons. ^g Three equivalent protons, probably the 7-*syn*-methyl group. ^h Seventeen of the expected 19 lines observed.

the semiquinone type²



Their stability involves the delocalization of the odd

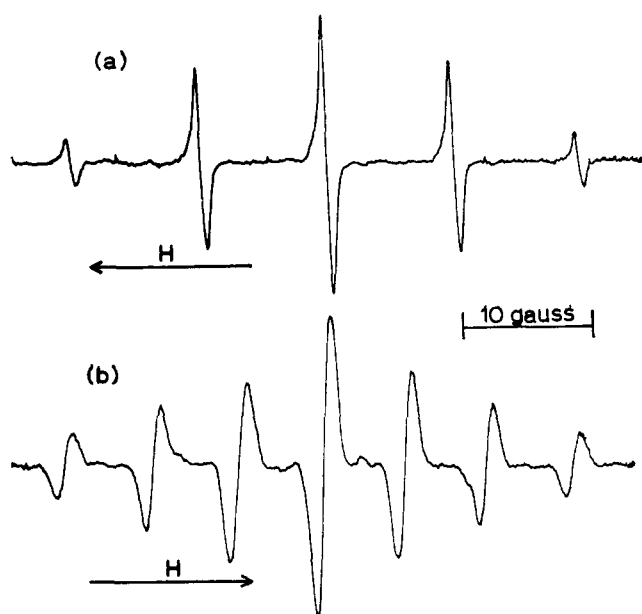


Fig. 1.—E.s.r. spectra of cyclohexane-1,2-dione radical anions ($\sim 1 \times 10^{-4}$ *M*) prepared by oxidation of (a) cyclohexanone or 2-hydroxycyclohexanone and (b) 4-*t*-butyl-2-hydroxycyclohexanone in the presence of base.

solutions while the electron-transfer experiments require the exclusion of oxygen.

Treatment of a mixture of 3,3,6,6-tetramethylcyclohexane-1,2-dione and 3,3,6,6-tetramethyl-2-hydroxycyclohexanone³ with base in dimethyl sulfoxide (80%)–*t*-butyl alcohol (20%) gave a radical-anion without hyperfine splitting. Figure 1 shows the spectra of the oxidation products of (a) 2-hydroxycyclohexanone or cyclohexanone and (b) 4-*t*-butylcyclohexanone. The unsubstituted compound has four equivalent α -hydrogens with a hyperfine splitting constant (hfsc) of $a_{\text{H}} = 9.82$ gauss, peak height ratios = 1:3.8:6:3.8:1. This cyclohexene derivative does not possess conformational stability in terms of the spectrometer frequency ($\sim 10^4$ Mc./sec.). However, the substitution of a *t*-butyl group gives rise to a conformationally stable radical-anion with peak height ratios (1:2:3:5.2:2.9:2:1) in good agreement with the ratios expected for two pairs of protons with $a_{\text{H}} = 13.10$ and 6.55 gauss. The average of these hfsc values is exactly the value obtained for the protons in the unsubstituted radical-anion.

The hfsc values for protons attached to a carbon atom adjacent to a carbon atom carrying a free electron are believed to satisfy the equation, $a_{\text{H}} = B\rho \cos^2 \theta$, where θ is the dihedral angle between the H–C $_{\alpha}$ –C $_{\pi}$ and the C $_{\alpha}$ –C $_{\pi}$ – π orbital planes and ρ is the spin density on C $_{\pi}$.⁴

(1) Reactions of Resonance Stabilized Anions. XII. Supported by the National Science Foundation.

(2) (a) B. Venkataramen and G. K. Frankel, *J. Am. Chem. Soc.*, **77**, 2707 (1955); (b) G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **84**, 4155 (1962); (c) R. Dehl and G. K. Frankel, *J. Chem. Phys.*, **39**, 1793 (1963).

(3) Kindly supplied by Professor D. E. Applequist.

(4) C. Heller and H. M. McConnell, *J. Chem. Phys.*, **32**, 1535 (1960).