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 Resonance[1]

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 $[C_6H_5COCHCH_3]^-$ (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 axial	equatorial	$\theta_{\text{axial-H}}$	$B\rho$	ρ^b
Cyclopentane-1,2-dione	1		14.16^c	$(+27)^{c,d}$	17.8	0.30
4-t-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	$a_{\text{methylene-H}} = 3.42$				
t-Butylphenylglyoxal	2	$a_{\text{methyl-H}} = 0.17$				
Di-t-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 type[2]

$$\underset{\text{Ar—C=C—Ar}}{\overset{\text{O· O}^-}{\overset{|\ \ |}{}}}$$
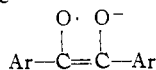
Their stability involves the delocalization of the odd
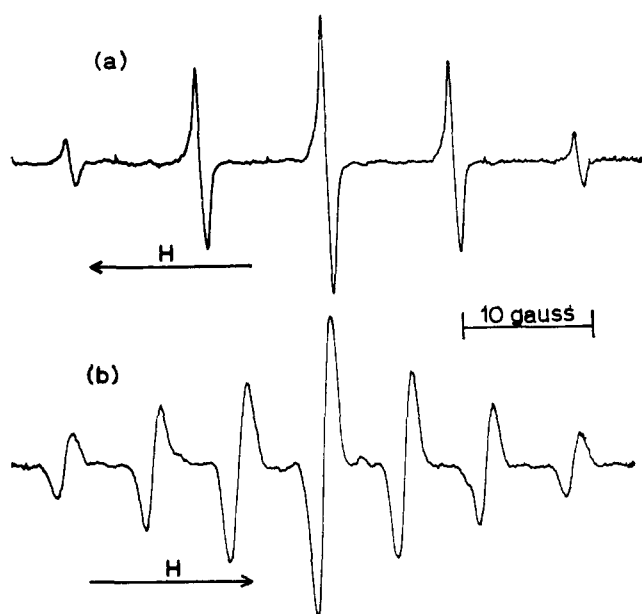

(a)

H ←

| 10 gauss |

(b)

H →

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-hydroxycyclohexanone[3] 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 $a_H = 9.82$ 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 $a_H = 13.10$ 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, $a_H = B\rho \cos^2 \theta$, where θ is the dihedral angle between the H–C_α–C_π and the C_α–C_π–π_{orbital} planes and ρ is the spin density on C_π.[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).
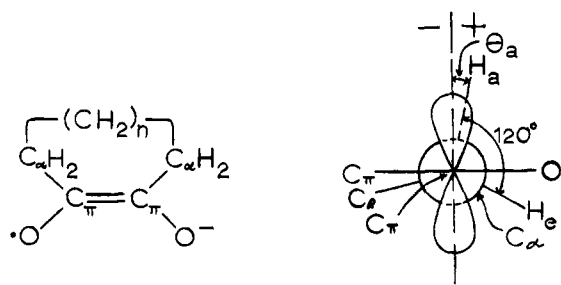
For the ethyl radical, B has a value of 58.5 gauss.[5] Solution of the equations, $a_{axial-H} = B\rho \cos^2 \theta_{axial}$, $a_{equat-H} = B\rho \cos^2 \theta_{equat}$, and $\theta_{equat-H} = \theta_{axial-H} + 120°$ (tetrahedral α-carbon atom) gives the results listed in Table I.[6] It is interesting that the value of θ_{axial} for the α-hydrogens of the 4-t-butylcyclohexane-1,2-dione radical-anion is the same as found for cyclohexene by n.m.r.[7]

Our results demonstrate the application of e.s.r. to conformational analysis of nonrigid systems and suggest the use of e.s.r. for structural determinations of rigid ketonic systems, such as the steroidal ketones. Work in this area is in progress.

(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963). These authors determined $Q\beta$ (CH₃). Since $\cos^2 45°$ (free rotation) is $1/2$, B is twice their value of $Q\beta$ (CH₃).

(6) Two values of $B\rho$ and two values of θ (except when $\cos^2 \theta_{equat-H} = 0$) are obtained. Unrealistic solutions ($B\rho > 58.5/2$) have not been listed.

(7) G. V. Smith and H. Kriloff, *J. Am. Chem. Soc.*, **85**, 2016 (1963). These authors use a dihedral angle for axial hydrogens equivalent to 90° $- \theta_a$.

(8) (a) Alfred P. Sloan Foundation Fellow, 1959–1963; (b) National Institutes of Health Predoctoral Fellow, 1962–1963.

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Photoisomerization of Azomethane

Sir:

Although *cis–trans* isomerization is well-established for aromatic azo compounds,[1,2] it has not been observed in the aliphatic series. We wish to report experiments in which the photochemical *cis–trans* isomerization of azomethane and the isolation of pure *cis*-azomethane have been achieved.
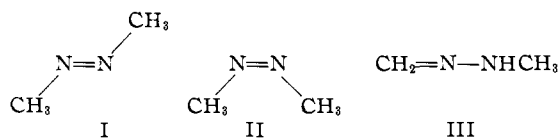
Azomethane (I), which exists in the *trans* configuration,[3–5] photolyzes readily in the gas phase, yielding nitrogen and two methyl radicals. In agreement with previous work,[6] the quantum yield (ϕ_{N_2}) for the photolytic decomposition of gaseous azomethane (I) by 365-mμ light was found to be 1.0 ± 0.1. In marked contrast, the quantum yield decreases dramatically when azomethane is irradiated in solution. Thus, for carefully degassed 5×10^{-3} M solutions in isooctane, ethanol, N,N-dimethylformamide, and water at 25°, the quantum yields, determined by nitrogen formation,

(1) G. Zimmerman, L. Chow, and U. Paik, *J. Am. Chem. Soc.*, **80**, 3528 (1958); E. Fischer, *ibid.*, **82**, 3249 (1960).

(2) *cis* and *trans* isomers of difluorodiazine (N₂F₂) are known: C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger, and C. O. Parker, *ibid.*, **81**, 6397 (1959); J. H. Noggle, J. D. Baldeschwieler, and C. B. Colburn, *J. Chem. Phys.*, **37**, 182 (1962).

(3) W. West and R. B. Killingsworth, *ibid.*, **6**, 1 (1938).

(4) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Company, Inc., Princeton, N. J., 1945, p. 357.

(5) I. D. Brown and J. D. Dunitz, *Acta Cryst.*, **13**, 28 (1960).

(6) E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1954, p. 376.

were, respectively, 0.17 ± 0.01, 0.07 ± 0.01, 0.05 ± 0.01, and 0.01 ± 0.01. In addition, fluorescence was not detected in any of these solutions.

However, chemical transformation does attend irradiation of azomethane in degassed solution and can be observed by ultraviolet absorption and by proton magnetic resonance spectroscopy. A solution of azomethane (I, 10^{-2} to 10^{-1} M) in degassed D_2O shows a single sharp resonance lying at δ +0.984 p.p.m.,[7] and is indefinitely stable in the dark at room temperature. Upon irradiation of the solution at room temperature, a new sharp singlet (II) appears 0.10 p.p.m. to high field from the resonance of I. By following the ratio of the height of the new resonance (II) to that of I as a function of irradiation time, it can be demonstrated that a photochemical equilibrium

$$I \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} II$$
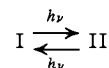
is established. Experiments using D_2O as solvent reveal no proton–deuteron exchange with the solvent while coming to and remaining at photochemical equilibrium. This, together with the simplicity of the spectrum of II, demands magnetic equivalence of all the protons of II.

A degassed aqueous solution of I has an absorption maximum at 343 mμ (ϵ 25); irradiation with 365-mμ light results in a shift of the apparent maximum to longer wave lengths with a concomitant increase in the optical density maximum(ΔD_{max}). Plots of ΔD_{max} *vs.* time of irradiation confirm the attainment of photochemical equilibrium, the band undergoing a 70% increase in ΔD_{max} with the establishment of the new maximum at 350 mμ.

From the photochemical steady-state areas of the proton resonance peaks, $K_{D_2O} = [II]/[I] = 0.09 ± 0.01$, for 365-m$\mu$ light. Under basic conditions II reacts (*vide infra*) at least 100 times faster than I, so that it can be removed selectively from solution. This permits an independent spectrophotometric determination of K, which, over a tenfold concentration range (5×10^{-3} to 5×10^{-2} M) has a value of 0.10 ± 0.01, in agreement with the proton resonance method.

Additionally, optical density measurements show that methanol, ethanol, and ethyl ether permit attainment of equilibrium with little photolytic decomposition. In methanol, the equilibrium is insensitive to temperature over the range −40 to +30°. Indeed, II is even formed on irradiation of an ether glass of I at −196°. The production of II also can be observed in carbon tetrachloride, toluene, and isooctane, although photochemical equilibrium cannot be reached because of concomitant decomposition.

If a solid thin film of pure I is irradiated at −196°, II is formed. Unisomerized I together with the very small amounts of ethane and nitrogen formed by photolytic decomposition may be removed by vacuum distillation at −78°. Further fractionation at *ca.* −50° provides II as a colorless liquid of m.p. −53 to −49°.

II, dissolved in D_2O, shows the expected single sharp proton resonance at 1.08 p.p.m. to high field from HDO. Irradiation of this solution gives back I; there is no dark reversion of II to I. The absorption spectrum of an aqueous solution of II has a maximum at 353 mμ (ϵ 240).[8] The value, $K^{365 m\mu} = 0.09$, calculated from the

(7) Chemical shifts are expressed in p.p.m. displacement (negative to low field, positive to high field) from the solvent HDO resonance. (A dilute solution of azomethane in CCl₄ shows its resonance at 3.67 ± 0.02 p.p.m. to low field from internal tetramethylsilane.)

(8) The molar extinction coefficient and λ_{max} accord with values obtained from the literature for cyclic aliphatic azo compounds constrained to a *cis* configuration: S. G. Cohen, R. Zand, and C. Steel, *J. Am. Chem. Soc.*, **83**, 2895 (1961); S. G. Cohen and R. Zand, *ibid.*, **84**, 586 (1962); C. G. Overberger, J. P. Anselme, and J. R. Hall, *ibid.*, **85**, 2752 (1963).