Table I. Chlorine Kinetic Isotopic Effects for the Cyclization of Chloroalcohols in Water at 25°[a]

Chloroalcohol	Base	k_2, M^{-1} sec^{-1}	Isotope effect (k_{35}/k_{37})
2-Chloroethanol	$(CH_3)_4N^+HO^-$	1.13×10^{-2}	1.00815 ± 0.00011[b]
4-Chlorobutanol	$(CH_3)_4N^+HO^-$	1.70×10^{-3}	1.00757 ± 0.00015[b]
4-Chlorobutanol	H_2O	2.86×10^{-8}	1.00796 ± 0.00013[b]

[a] 4-Chloroethanol and hydroxide each initially 0.03–0.08 *M*. [b] Standard deviation of five–seven independent determinations.

Table II. Kinetic Data for the Cyclization of 4-Chlorobutanol in Water at 25°[a]

Base	pK_A[b]	k_2, M^{-1} sec^{-1}
$(CH_3)_4N^+HO^-$	14.00	1.70×10^{-3}
$Na^+F_3CCH_2O^-$	12.37[c]	1.80×10^{-4}
$Na^+C_6H_5O^-$	9.97	3.88×10^{-5}
$Na^+4\text{-}O_2NC_6H_4O^-$	7.17	1.83×10^{-6}
$Na^+2,4,6\text{-}Cl_3C_6H_2O^-$	6.41	1.97×10^{-6}
$Na^+2,4\text{-}(O_2N)_2C_6H_3O^-$	4.09	4.48×10^{-7}
H_2O	−1.74	2.86×10^{-8} [d]

[a] 4-Chlorobutanol initially 0.004–0.08 *M*; basic solutes 0.1–0.4 *M*; $NaClO_4$ to make ionic strength 0.45 *M*. [b] R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc., Ser. A*, **197**, 141 (1949). [c] P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **81**, 1050 (1959). [d] Calcd for 55.5 *M* water.

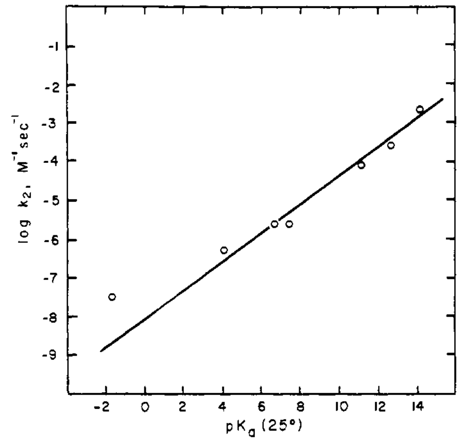


Figure 1. Brønsted plot for the cyclization of 4-chlorobutanol in water at 25°. Data points (left to right) correspond to water, 2,4-dinitrophenoxide, 2,4,6-trichlorophenoxide, 4-nitrophenoxide, phenoxide, 2,2,2-trifluoroethoxide, and hydroxide. The Brønsted β of 0.36 was determined by least-squares analysis excluding the datum for water.

of ethylene oxide, than even the fully protonated oxygen atom of tetrahydrofuran. Therefore, the oxygen atom of 2-chloroethoxide must be a poorer nucleophile (albeit a stronger base) than the partially deprotonated oxygen atom in the transition state for the cyclization of 4-chlorobutanol. The entropic difference between the two ring closures allows the cyclization with the weaker nucleophile (2-chloroethoxide) to occur more readily than that of the stronger nucleophile (the partially deprotonated 4-chlorobutanol).

The original claim of general base catalysis for the cyclization of 4-chlorobutanol rested on a Brønsted plot including only one base other than water and hydroxide. Although general base catalysis for this reaction has been confirmed,[9] we redetermined the Brønsted slope for this cyclization with a series of oxygen bases. The results of this study are presented in Figure 1 and Table II. The reaction in water is ten times faster than predicted from the basicity of water and the best line determined by the other bases, a deviation well outside experimental error. Although water and hydroxide ion often deviate in Brønsted plots (though not in all[10]), the fact that only water was observed to do so in this system led us to determine the chlorine kinetic isotope effect for the neutral cyclization of 4-chlorobutanol. Comparison of the second and third entries of Table I shows that the isotope effects for the hydroxide ion and water reactions are different with a confidence limit above 99% by Student's *t* test. The difference in chlorine isotope effects requires that the carbon–chlorine, and therefore the carbon–oxygen, bonding be different in the transition states for the two reactions. Moreover, the relative magnitudes for the isotope effects demonstrate that the transition state for the hydroxide ion catalyzed reaction has less weakening of the carbon–chlorine bond, *i.e.*, occurs earlier along the reaction coordinate. Two explanations equally well account for the isotope effect data and the apparent curvature of the Brønsted plot. The cyclization in water may represent the rather abrupt onset of a cyclization in which water does not act as a general base.[10] In this case the cyclization is an uncatalyzed ring closure to a fully protonated tetrahydrofuran from which the proton is lost in a subsequent fast step. A more likely alternative is that the transition state for the cyclization is gradually changing in response to the difference in p*K* between the base and the alcohol.[11] Both explanations predict an earlier transition state for the hydroxide-catalyzed cyclization and distinction between them must await further experimentation.

Acknowledgment. This research was supported in part by a research grant from the National Science Foundation.

References and Notes

(1) C. G. Swain, D. A. Kuhn, and R. L. Schowen, *J. Amer. Chem. Soc.*, **87**, 1553 (1965).
(2) W. P. Jencks, "Catalysis in Chemistry and Enzymology," McGraw-Hill, New York, N.Y., 1969, pp 169–170.
(3) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, Wiley, New York, N.Y., 1961, pp 288–307.
(4) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).
(5) W. P. Jencks, ref 3, pp 193–199.
(6) C. G. Swain and E. R. Thornton, *J. Amer. Chem. Soc.*, **84**, 817 (1962).
(7) For experimental procedures, see T. M. Bare, N. D. Hershey, H. O. House, and C. G. Swain, *J. Org. Chem.*, **37**, 997 (1972); for further details see T. H. Cromartie, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, Mass., 1973.
(8) A. Fry in "Isotope Effects in Chemical Reactions," C. J. Collins and N. S. Bowman, Ed., Van Nostrand-Reinhold, New York, N.Y., 1970, Chapter 6; S. E. Schepple, *Chem. Rev.*, **72**, 511 (1972); J. Bigeleisen and M. Wolfsberg, *Advan. Chem. Phys.*, **1**, 15 (1958).
(9) W. P. Jencks, unpublished observations quoted in ref 2.
(10) D. S. Kemp and M. L. Casey, *J. Amer. Chem. Soc.*, **95**, 6670 (1974).
(11) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3**, 1 (1964); M. Eigen, *Discuss. Faraday Soc.*, **No. 39**, 7 (1965).
(12) National Science Foundation Predoctoral Fellow, 1969–1973.

Thomas H. Cromartie,[12] C. Gardner Swain*
Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Received September 12, 1974

Electron Paramagnetic Resonance Spectra and Structure of Some Vinyl Radicals in Solution[1]

Sir:

Almost all types of carbon-centered radicals have been studied extensively in solution by epr spectroscopy. How-

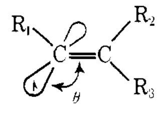
Table I. Epr Parameters for Some Vinyl Radicals in Solution at 25° (Hyperfine Splittings in Gauss)

Radical	g^{a}	$a^{\mathrm{H}\gamma\ a}$	$a^{^{29}\mathrm{Si}\beta}$	$a^{^{29}\mathrm{Si}\gamma}$	$a^{\mathrm{H}\delta,\epsilon\ b}$	a^{other}
$Me_3C\dot{C}{=}C(H)SiMe_3$	2.0020	67.6		$(22.8)^{c}$	0.33_8	
$Me_3Si\dot{C}{=}C(H)SiMe_3$	2.0023	72.4	*d*	*d*	*e*	
$Me_3Si\dot{C}{=}C(SiMe_3)_2$	2.0022		8.5	49.7^{f}	0.25_3	$a^{^{13}\mathrm{C}\alpha} = 28.1$
$Me_3Si\dot{C}{=}C[(EtO)_2PO]SiMe_3$	2.0023		13.7	34.7_5	*e*	$a^{^{13}\mathrm{C}\alpha} < 35$; $a^{^{31}\mathrm{P}\gamma} = 164.1^{a}$
$Me_3Si\dot{C}{=}C(CF_3)SiMe_3{}^{g}$	2.0025		9.9_5	28.2	0.42	$a^{^{13}\mathrm{C}\alpha} = 47.7^{h}$
$Me_3Si\dot{C}{=}C(OCF_3)SiMe_3$	2.0021		12.1	19.0	0.37_4	$a^{^{19}\mathrm{F}\epsilon} = 12.4$ (3 F)
$H\dot{C}{=}CH_2{}^{i}$	2.0022	68.0 34.0				$a^{\mathrm{H}\alpha} = 16.0$, $a^{^{13}\mathrm{C}\alpha} = 107.5$

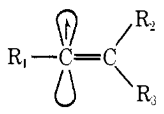
[a] Corrected using the Breit–Rabi equation. [b] Data quoted are the line spacings in the hyperfine slitting patterns that are produced by both δ and ϵ hydrogens. The individual splittings due to δ-H and ϵ-H were not identified. [c] Tentative identification. Only one of the lines is visible, the other (if present) being "masked" by lines from "contaminating" radicals. [d] Too weak for detection. [e] Not resolved. [f] Due to two equivalent silicons. [g] Fluorine splitting was not identifiable, presumably because it is a small multiple of 0.42 G (*i.e.*, $a^{\mathrm{F}} = 0.42, 0.84$, or 1.26 G). [h] Assigned to C_α rather than to C_γ because of the small value of a^{F}. [i] From ref 3a and 6.

ever, vinyl radicals are an exception, presumably because of their high reactivity toward the nonradical components of the solution.[2] This observational problem may be overcome by generating the radicals extremely rapidly, and preferably at a low temperature. In this way, Fessenden and Schuler[4] obtained the epr spectra of vinyl and of 1-methylvinyl, the only neutral vinyls that have up to now been detected in solution. An alternative approach that has proved effective with a wide variety of radicals is to reduce reactivity by placing bulky groups around the radical center.[5] We wish to report the successful application of this procedure to vinyl radicals (see Table I).

It has been shown by epr[3a,b,4,6-8] that vinyls can be classified either as "bent," **1**, with the unpaired electron in an orbital with substantial s character (*e.g.*, 1-methylvinyl), or as "linear," **2**, with the unpaired electron in a pure p orbital when the α substituent R_1 is capable of delocalizing the unpaired spin, *e.g.*, 1-phenylvinyl.[3f,g,8,9]



1

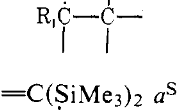


2

Both $Me_3C\dot{C}{=}C(H)SiMe_3$ and $Me_3SiC{=}C(H)SiMe_3$ have H_γ splittings[10] close to that reported for the γ-H of vinyl that is trans to the unpaired electron (*viz.*, 68 G).[3a] The two bulky substituents therefore take up a trans configuration with respect to one another as we would expect on steric grounds, *i.e.*, structure **1** with $R_2 = H$.

The more highly hindered $Me_3Si\dot{C}{=}C(SiMe_3)_2$ radical must adopt structure **2** since the two γ silicons are magnetically equivalent. This equivalence is probably not due to rapid inversion at C_α of a "bent" radical since the silicons remain equivalent at temperatures as low as −130°. Furthermore, the value of $a^{^{13}\mathrm{C}\alpha}$ is typical of that for a planar alkyl radical (*e.g.*, 38.3 G for $\dot{C}H_3$[6] and 26 ± 3 G for $(Me_3Si)_3\dot{C}$[11]), whereas for vinyl itself $a^{^{13}\mathrm{C}\alpha} = 107.6$ G.[6]

In $R\dot{C}{=}CH_2$ radicals having structure **2**, the two (equal) γ-H couplings are of similar magnitude to those found for a γ-H which eclipses the $C_\alpha 2p_z$ orbital in an analogous ethyl radical [3f,g]



$$R_1\dot{C}{-}C(H){-}$$

However, in $Me_3SiC{=}C(SiMe_3)_2$ $a^{\mathrm{Si}\gamma}$ (49.7 G) is significantly greater than in $\dot{C}H_2CH_2SiEt_3$ (37.4 G)[12,13] or $(Me_3C)_2\dot{C}CH_2SiMe_3$ (35 G).[13,14] Presumably, with substituents larger than H, shortening of the C_α–C_β bond produces an appreciable improvement in overlap of the $C_\alpha 2p_z$ orbital and the C_β–Si_γ σ-bonds.

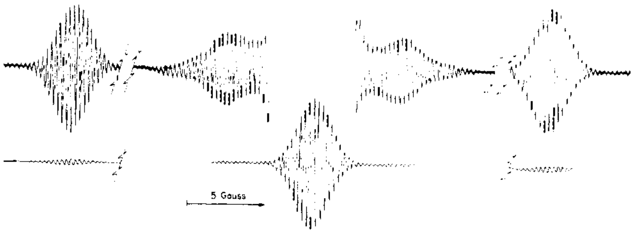


Figure 1. Epr spectrum of $Me_3Si\dot{C}{=}C(SiMe_3)_2$ at 25° in $Me_3COOCMe_3$. Top spectrum run at 20× gain of lower spectrum.

The additional radicals listed in Table I have been chosen to show the types of vinyl we have prepared, rather than to illustrate specific structural effects. A full discussion of epr parameters will be given in the full paper. However, we would like to point out that the epr parameters of these vinyls mirror in magnitude and trends the parameters for $(Me_3C)_2\dot{C}CH_2MR_n$ radicals.[14] This similarity is not entirely unexpected since, for steric reasons, the $(Me_3C)_2\dot{C}CH_2MR_n$ radicals hold the MR_n group in the eclipsed position relative to the $C_\alpha 2p_z$ orbital,[14] *i.e.*, in a similar conformation to that obtaining in structure **2** vinyls.

The exceptionally fine epr spectra (see Figure 1) obtained with our vinyls are a consequence of their relatively long lifetimes ($\tau_{1/2} \sim$ minutes in some cases), and these in turn are a consequence of steric shielding of the reaction center.[5] For example, $Me_3Si\dot{C}{=}C(OCF_3)SiMe_3$ has a second-order decay rate constant of $2.5 \times 10^3\ M^{-1}\ \mathrm{sec}^{-1}$ at 0°, which corresponds to a half-life at $10^{-5}\ M$ of about 1 min.

References and Notes

(1) Issued as N.R.C.C. No. 14428.
(2) A number of vinyls have been trapped on or in solids at low temperatures.[3]
(3) See, *e.g.*, (a) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **40**, 213 (1964); (b) F. J. Adrian and M. Karplus, *ibid.*, **41**, 56 (1964); (c) P. H. Kasai and E. B. Whipple, *J. Amer. Chem. Soc.*, **89**, 1033 (1967); (d) S. Fenistein, R. Marx, C. Moreau, and J. Serre, *Theor. Chim. Acta*, **14**, 339 (1969); (e) M. Iwasaki and B. Eda, *J. Chem. Phys.*, **52**, 3837 (1970); (f) J. E. Bennett and J. A. Howard, *Chem. Phys. Lett.*, **9**, 460 (1971); (g) L. Bonazzola, S. Fenistein, and R. Marx, *Mol. Phys.*, **22**, 689 (1971); (h) G. W. Nielson and M. C. R. Symons, *J. Chem. Soc., Perkin Trans. 2*, 1405 (1973).
(4) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).
(5) G. D. Mendenhall, D. Griller, and K. U. Ingold, *Chem. Brit.*, **10**, 248 (1974).
(6) R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967).
(7) P. Millié, B. Lévy, and G. Berthier, *Int. J. Quantum Chem.*, **6**, 155 (1972).
(8) R. M. Kochik and J. A. Kampmeir, *J. Amer. Chem. Soc.*, **90**, 6733 (1968).
(9) See also L. A. Singer and J. Chen, *Tetrahedron Lett.*, 4849 (1969).
(10) Positions in the vinyls are designated as in the following example $H_\delta C_\gamma Si_\beta \dot{C}_\alpha{=}C_\beta(H_\gamma)Si_\gamma C_\delta H_\epsilon$.
(11) A. R. Bassindale, A. J. Bowles, M. A. Cook, C. Eaborn, A. Hudson, R. A. Jackson, and A. E. Jukes, *Chem. Commun.*, 559 (1970).

(12) T. Kawamura and J. K. Kochi, *J. Amer. Chem. Soc.*, **94**, 648 (1972).
(13) Silicon eclipses the $C_\alpha 2p_z$ orbital.
(14) D. Griller and K. U. Ingold, *J. Amer. Chem. Soc.*, **95**, 6459 (1973); **96**, 6715 (1974).
(15) N.R.C.C. Summer Student 1974.
(16) N.R.C.C. Postdoctoral Fellow 1973–1975.

J. W. Cooper,[15] D. Griller,[16] K. U. Ingold*
Division of Chemistry, National Research Council Canada
Ottawa, Ontario, K1A OR9, Canada

Received September 24, 1974

Reversible Carbon Monoxide Binding by Ruthenium Carbonyl Porphyrins

Sir:

There have been a number of recent reports of reversible complexation of carbon monoxide by iron(II)[1-3] and cobalt(II)[4] porphyrins. We now report the preparation of ruthenium(II) carbonyl porphyrin complexes which exhibit reversible carbon monoxide binding, and the isolation of an analytically pure dicarbonyl complex.

Octaethylporphyrin,[5,6] $Ru(CO)(CF_3TPP)(THF)$,[7] $Ru(CO)(TPP)(EtOH)$,[8] and $Ru(CO)(i\text{-}PrTPP)(EtOH)$[8] were prepared as reported. $Ru(CO)(OEP)(THF)$[9,10] was prepared by refluxing 500 mg of $Ru_3(CO)_{12}$ and 500 mg of H_2OEP in 125 ml of dry toluene for 9 hr in a nitrogen atmosphere. After removal of the toluene *in vacuo*, the residue was extracted with benzene. The benzene solution was chromatographed on Baker 0537 alumina. Impurities were eluted with benzene, and the complex was eluted with 1:30 THF:benzene. After removal of the solvent the product was recrystallized from trichloroethylene–heptane, yield 520 mg, $\nu_{CO} = 1950\ cm^{-1}$: visible spectrum in benzene (log ϵ in parentheses), 549 (4.55), 517 (4.21), 394 (5.36), 375 sh (4.71); pmr in $CDCl_3$, CH_3, 1.92 triplet; CH_2, 4.01 quartet; pyrrole, 9.91 singlet; THF −1.23, −0.45, multiplets. The ethanol adduct, $Ru(CO)(OEP)(EtOH)$, was prepared analogously using EtOH–benzene as eluant in the chromatographic purification.

Benzene solutions of $Ru(CO)(OEP)(THF)$ or $Ru(CO)(OEP)(EtOH)$ exposed to a CO atmosphere precipitate a brick red complex within a few minutes. Volume reduction in a stream of CO affords a 90–95% yield of the dicarbonyl complex ($\nu_{CO} = 1990\ cm^{-1}$). Dicarbonyl ruthenium complexes of TPP, *i*-PrTPP, and CF_3TPP were similarly prepared using trichloroethylene or benzene as solvents. The slightly soluble red complexes were filtered off and dried at reduced pressure in a CO atmosphere; $\nu_{CO} = 2005$, 1995, and $2050\ cm^{-1}$, respectively. The carbonyl stretching frequency range of $1990\text{–}2050\ cm^{-1}$ for these ruthenium dicarbonyl porphyrin complexes is higher than the range of $1920\text{–}1960\ cm^{-1}$ observed for ruthenium monocarbonyl porphyrin complexes,[11-13] as expected on the basis of competition of trans carbonyls for the metal orbitals.

$Ru(CO)_2(TPP)$, $Ru(CO)_2(i\text{-}PrTPP)$, and $Ru(CO)_2(CF_3TPP)$ readily lose CO upon standing and during grinding of samples for infrared studies. When halocarbon oil mulls of these compounds were prepared in a CO atmosphere a strong peak attributed to the dicarbonyl species and a very weak peak attributed to the monocarbonyl species were observed. Further grinding of the sample in a dry nitrogen atmosphere resulted in a rapid loss of the dicarbonyl peak and an increase in the relative intensity of the monocarbonyl peak. Return of the sample to a CO atmosphere resulted in growth of the dicarbonyl peak and diminution of the monocarbonyl peak. These changes were fully reversible several times. Exposure to air yielded a third peak which increased in relative intensity with continued grinding. Comparison with independently prepared samples indicated that this peak was due to the monocarbonyl complex with water in the sixth coordination site. A complex identified as $Ru(CO)_2(TPP)$ was previously reported[14] but was subsequently shown to be $Ru(CO)(TPP)(EtOH)$.[8]

$Ru(CO)_2(OEP)$, the most stable of the dicarbonyl complexes studied, could be kept under high vacuum overnight without loss of CO. However, one CO is rapidly and quantitatively replaced by 4-*tert*-butylpyridine (*t*-Bu(py)). In a typical experiment 17 mg (2.47×10^{-5} mol) of $Ru(CO)_2(OEP)$ was placed in a 2.5-ml reaction vessel closed with a serum stopper and connected to a capillary mercury manometer. The system was evacuated and isolated. Then 0.25 ml of *t*-Bu(py) was introduced by syringe. Vigorous bubbling ensued reaching equilibrium within about 1 hr. The pressure change corresponded to 1.00 ± 0.05 mol of gas evolved per mole of complex. The solid formed was filtered, washed with hexane, and characterized as $Ru(CO)(OEP)(t\text{-}Bu(py))$ by ir ($\nu_{CO} = 1935\ cm^{-1}$), nmr, and elemental analysis. The gas evolved from a 100-mg sample in a similar experiment using a small reaction vessel connected to a 100×25 mm gas cell with NaCl plates was identified as CO by the rotational fine structure of the gas phase ir spectrum. One carbonyl can also be displaced from $Ru(CO)_2(OEP)$ by other bases such as H_2O.

The strength of binding of the second carbonyl increases in the order $CF_3TPP < i\text{-}PrTPP \sim TPP \ll OEP$. This is consistent with observations on iron porphyrin carbonyl complexes, (piperidine)Fe(CO)(porphyrin), in which CO is more strongly bound by the protoporphyrin IX complex than by the TPP complex.[1]

During the purification steps the ruthenium carbonyl porphyrins usually pick up bases such as water, tetrahydrofuran or ethanol as has been reported previously.[8,11-13] Thus the ruthenium carbonyl porphyrin complexes commonly have a base in the sixth coordination site. The preparation of dicarbonyl complexes followed by removal of the second carbonyl group *in vacuo* provides a route to complexes with a vacant sixth coordination site.

Nonequivalence of the phenyl ring protons in the pmr spectra of Ru(CO)(RTPP) complexes with various bases in the sixth coordination site has been described.[13] Averaging of the nonequivalent proton peaks due to restricted rotation of phenyl rings has been reported for several porphyrin complexes.[13,15-19] In the case of indium chloroporphyrins[18] and iron haloporphyrins,[17] averaging of the phenyl resonances due to axial halogen exchange has been observed under certain conditions. Addition of CO to samples of $Ru(CO)(i\text{-}PrTPP)(THF)$ results in similar averaging of the nonequivalent phenyl proton resonances indicating that CO exchange is rapid at ambient temperature when excess CO is present in solution.

Further aspects of the interaction of ruthenium porphyrin complexes with CO, phosphines, and other small molecules will be reported in detail later.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

References and Notes

(1) D. V. Stynes, H. C. Stynes, B. R. James, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 4087 (1973).
(2) J. P. Collman, R. R. Gagne, T. R. Halbert, J.-C. Marchon, and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 7868 (1973); J. P. Collman, R. R. Gagne, and C. A. Reed, *ibid.*, **96**, 2629 (1974).
(3) C. K. Chang and T. G. Traylor, *J. Amer. Chem. Soc.*, **95**, 5810, 8475, 8477 (1973); *Proc. Nat. Acad. Sci. U. S.*, **70**, 2647 (1973).
(4) B. B. Wayland and D. Mohajer, *J. Amer. Chem. Soc.*, **93**, 5295 (1971); B. B. Wayland, J. V. Minkiewicz, and M. E. Abd-Elmageed, *ibid.*, **96**,