potential of acetic acid is located more positively than the valence band edge of CdS. The situation in the case of lactic acid looks similar to the case of acetic acid. Because the valence band of TiO_2 is located deeply enough to oxidize carboxylate, decarboxylation could occur for TiO_2. On the other hand, the valence band of CdS is located less deeply than that of TiO_2. Therefore CdS photocatalyst could oxidize only the OH group of lactic acid. At the present stage of research this is an assumption, but it seems reasonable. In addition to the above reason, the difference in the adsorption properties of lactic acid to the surface of TiO_2 and CdS would also be important. Anyway, the above results suggest the possibility of controlling photocatalytic reactions by selecting a semiconductor with a suitable oxidizing power and adsorption property.

It is known that CdS suffers corrosion under irradiation.[7] In order to determine the amount of CdS dissolved during the photocatalytic reaction, cadmium was analyzed by atomic absorption spectroscopy. In the sample before irradiation, 0.1 mmol of Cd was detected. This quantity was not changed even after 130 h of irradiation. Since 28.3 mmol of hydrogen was produced during the reaction, more than 99.6% of the photogenerated holes were consumed for the photocatalytic reaction even if all of 0.1 mmol of Cd was assumed to have been produced from the photocorrosion.[8] In the analysis by polarography, the amount of Cd^{2+} was smaller than 3.6 μmol. These results indicate that the photocorrosion of CdS is negligibly small in the present reaction, suggesting a very rapid and efficient oxidation of lactic acid.

(6) Sakata, T.; Kawai, T. J. Synth. Org. Chem., Jpn. 1981, 39, 589.
(7) Kolb, O. M.; Gerischer, H. Electrochim. Acta 1973, 18, 987.
(8) Even when the solubility of CdS in water (1.46×10^{-10} mol/L) is taken into consideration, the amount of cadmium in the solution is unusually large. The following two reasons are most plausible. First, $CdSO_4$ or $CdCl_2$, which are used for manufacturing CdS, remained on the surface of particulate CdS. Second, very fine particles of CdS were not removed completely by the filter of 0.22-μm pore size used. These reasons might explain the discrepancy between the atomic absorption and polarographic analyses.

2,4-Dimethylene-1,3-cyclobutadiyl

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Received November 16, 1984

We report herein the direct observation of 2,4-dimethylene-1,3-cyclobutadiyl (**1**, alternatively 1,3-dimethylenecyclobutadiene) by ESR spectroscopy.


1
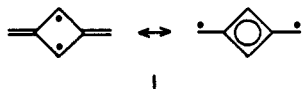
Biradical **1** is a non-Kekulé[2] C_6H_6 alternant hydrocarbon, which

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(2) (a) Dewar, M. J. S. "The Molecular Orbital Theory of Organic Chemistry"; McGraw-Hill: New York, 1969; pp 232–233. (b) See also: Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. Tetrahedron, 1982, 38, 787–798.

Scheme I[a]
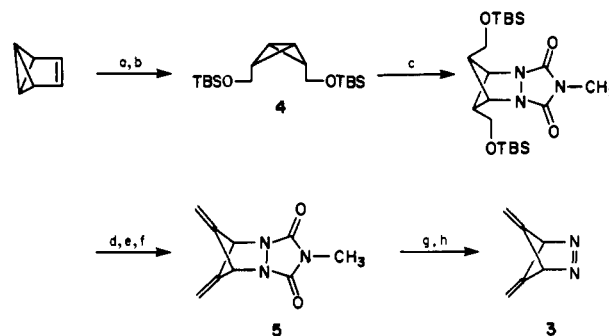
[a] (a) O_3, −78 °C; LiAlH$_4$, THF, −30 °C.   (b) t-BuMe$_2$SiCl, imidazole, CH_2Cl_2.   (c) MTAD, hν, pentane.   (d) n-Bu$_4$N$^+$F$^-$, THF.   (e) o-NO$_2$PhSeCN, n-Bu$_3$P, THF.   (f) O_3, $CHCl_3$, −65 °C; i-Pr$_2$NH, CCl_4, Δ.   (g) KOH, Me$_2$SO/H$_2$O.   (h) Nickel peroxide, CH_2Cl_2, −78 °C.

has been predicted by both simple[3] and sophisticated[4] theoretical models to possess a triplet ground state. Its covalent isomer, **2**,

2

is highly strained, and thus a significant barrier to ring closure could exist for both triplet and singlet **1**. This, in turn, could allow thorough spectroscopic and chemical characterization of this novel species.[5]

Diazene **3** is a logical precursor to **1**,[6] and its synthesis is shown in Scheme I. The key step in this sequence is the stereospecific *photochemical* addition[7] of N-methyltriazolinedione (MTAD) across the strained central bond of bicyclobutane derivative **4**.[8] Thus, the photochemical attack of MTAD occurs from the sterically congested endo face, as is the case for the thermal addition to the parent bicyclobutane.[9] Apparently, photochemical excitation enhances the reactivity of MTAD, since **4** is completely inert toward thermal addition. Subsequent removal of the protecting groups[10] and o-nitrophenyl selenoxide elimination[11] efficiently afforded diene **5**.[12] Although standard hydrolysis/oxidation procedures were unsuccessful, diazene **3** could be prepared by a novel two-step sequence involving first a partial hydrolysis of **5** to the semicarbazide.[13] Treatment of this compound with

(3) Roberts, J. D.; Streitwieser, A., Jr.; Regan, C. M. J. Am. Chem. Soc. 1952, 74, 4579–4582. Ovchinnikov, A. A. Theor. Chim. Acta 1978, 47, 297–304. Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, F. A. J. Chem. Phys. 1982, 77, 3101–3108.
(4) (a) Feller, D.; Davidson, E. R.; Borden, W. T. J. Am. Chem. Soc. 1982, 104, 1216–1218. (b) Davidson, E. R.; Borden, W. T.; Smith, J. J. Am. Chem. Soc. 1978, 100, 3299–3302. Borden, W. T.; Davidson, E. R. J. Am. Chem. Soc. 1977, 99, 4587–4594.
(5) For extensive studies of a related system, see: Berson, J. A. Acc. Chem. Res. 1978, 11, 446–453. Berson, J. A. In "Diradicals"; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 4, pp 151–194.
(6) Dowd, and Schappert recently reported that photolysis of 4,5-dimethylenebicyclo[1.1.1]pentan-2-one did not produce a triplet ESR signal. Schappert, R. F. Ph.D. Thesis, University of Pittsburgh, 1982.
(7) Amey, R. L.; Smart, B. E. J. Org. Chem. 1981, 46, 4090–4092.
(8) For the antecedent diol, see: Leininger, H.; Lanzendörfer, F.; Christl, M. Chem. Ber. 1983, 116, 669–680. Leininger, H.; Christl, M. Angew. Chem., Int. Ed. Engl. 1980, 19, 458–459.
(9) Chang, M. H.; Jain, R.; Dougherty, D. A. J. Am. Chem. Soc. 1984, 106, 4211–4217. Chang, M. H.; Dougherty, D. A. J. Org. Chem. 1981, 46, 4092–4093. Chang, M. H.; Dougherty, D. A. J. Am. Chem. Soc. 1982, 104, 1131–1132.
(10) Corey, E. J.; Venkateswarlu, A. J. Am. Chem. Soc. 1972, 94, 6190–6191.
(11) Grieco, P. A.; Gilman, S.; Nishizawa, M. J. Org. Chem. 1976, 41, 1485–1486. Sharpless, K. B.; Young, M. W. J. Org. Chem. 1975, 40, 947–949. Reich, H. J.; Renga, J. M.; Reich, I. L. J. Am. Chem. Soc. 1975, 97, 5434–5447.
(12) Isolated as a white solid, mp ca. 150 °C dec, after chromatography: ^{1}H NMR (C_6D_6) δ 4.50 (s, 2 H, CH), 4.37 (s, 4 H, CH_2), 2.50 (s, 3 H, NCH$_3$); ^{13}C NMR (CDCl$_3$) δ 161.6 (C=O), 137.4 (quat C), 100.9 (CH_2), 68.9 (CH), 25.9 (NCH$_3$); mass spectrum, m/e 191 (36), 134 (35), 106 (33), 78 (55), 52 (100). Anal. ($C_9H_9O_2N_3$) C, H, N.
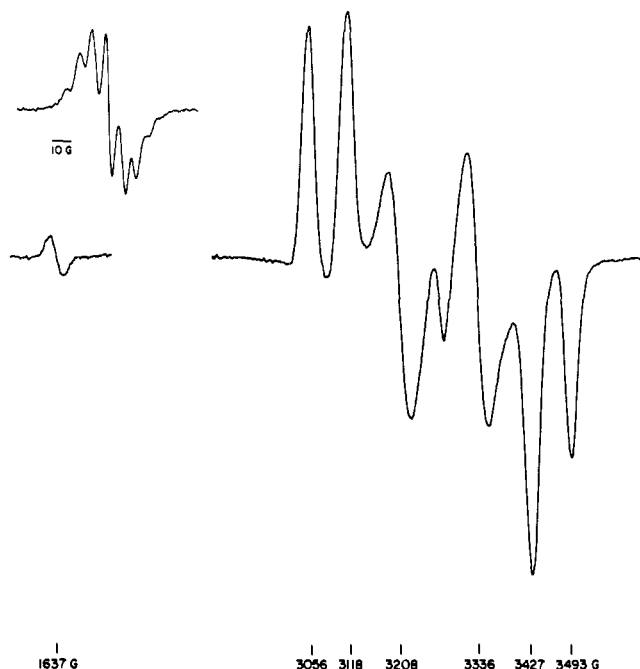(13) Jösel, R.; Schröder, G. Liebigs Ann. Chem. 1980, 1428–1437.

Figure 1. ESR spectrum of **1** observed after sensitized photolysis (λ 315–415 nm) of **3** in MTHF containing 0.27 M Ph$_2$CO at 10 K. The weak central line near 3270 G is assigned to a double-quantum transition based on its microwave power dependence.[18] Inset: hyperfine structure of the Δm_s = 2 transition (1637 G).

nickel peroxide[14] at −78 °C in CH$_2$Cl$_2$ afforded **3** as an unstable white solid.[15]

The ^{1}H NMR (CD$_2$Cl$_2$) spectrum of **3** at −75 °C exhibited singlets at δ 5.48 and 4.75 in a 1:2 ratio. These decreased with a 1 h half-life at −60 °C, with an accompanying increase in numerous signals associated with as yet uncharacterized products.[16] The ^{13}C NMR (CD$_2$Cl$_2$, −75 °C) signals of **3** at δ 157.7, 97.0, and 82.9 and the UV transition at 334 nm (MTHF) were also found to decay in this temperature range.

When a frozen solution of diazene **3** in 2-methyltetrahydrofuran (MTHF) is irradiated (λ 315–415 nm)[17] in the presence or absence of benzophenone at 10 or 77 K, the ESR spectrum of Figure 1 is obtained. The spectrum displays zero-field splitting parameters $|D/(hc)|$ = 0.0205 cm^{-1} and $|E/(hc)|$ = 0.0028 cm^{-1}. This D value is completely consistent with structure **1** on the basis of the spectra of a variety of other delocalized biradicals[2b] and a calculated value $|D/(hc)|$ = 0.026 cm^{-1}, obtained by using a previously described semiempirical method.[2b] The half-field transition (1637 G, Figure 1) shows a seven-line hyperfine splitting of 6–7 G,[19] indicating that the two sets of nonequivalent protons in **1** have similar hyperfine coupling constants. Although triplet **1** decomposes slowly at temperatures near 77 K, a preliminary Curie plot was linear, consistent with a triplet ground state.

Sensitized photolysis (λ 315–415 nm) of **3** in MTHF at 77 K produces a faint orange color. In addition, irradiation of triplet **1** (10 K) at λ 500 ± 15 nm causes irreversible destruction of the ESR signal within seconds, indicating that triplet **1** has a strong electronic transition in this region.

Identification of the thermal and photochemical products from **3** and trapping and spectroscopic studies of **1** are in progress.

Two-Dimensional ^{1}H–^{113}Cd Chemical-Shift Correlation Maps by ^{1}H-Detected Multiple-Quantum NMR in Metal Complexes and Metalloproteins

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The ^{113}Cd nucleus has received increasing attention as a spin $^1/_2$ NMR probe for the study of the structural and/or functional role of metal(s) in metalloproteins.[4–6] This is so in spite of the difficulties of low sensitivity, 1/100 that of protons when fully enriched, and comparatively long T_1's, due to the absence of directly bonded protons, which limit the rate of data accumulation. Furthermore, in certain motional regimes the negative gyromagnetic ratio of ^{113}Cd can also lead to nulling of signals under conditions of partial NOE. If spin coupling exists to a proton, then magnetization transfer experiments, such as INEPT or DEPT, where the shorter T_1 of the coupled proton determines acquisition rate, theoretically offer enhancements of (γ_H/γ_{Cd}) over direct Cd detection.[7,8] If, however, several protons are coupled to the nucleus one wishes to observe with comparable coupling constants, or if these protons are coupled to other protons, this enhancement is significantly reduced.[9]

Recently it has been shown that through proton indirect detection of ^{15}N via heteronuclear multiquantum coherences (HMQC's), enhancements on the order of $(\gamma_H/\gamma_N)^3$, 10^3-fold, can be achieved as theoretically predicted.[10] This approach has been applied to the enhancement of rare and low γ nuclei using direct one-bond ^{1}H–^{15}N (or ^{13}C) couplings (90 Hz or greater).[10–15] It can, in principle, be used with longer range couplings. This is of importance where no directly bonded proton is present, which is generally the situation for metal nuclei in organometallic complexes and metalloproteins. A pulse scheme related to that

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(4) Armitage, I. M.; Otvos, J. D. "Biological Magnetic Resonance"; Berliner, L. J., Reuben, J., Eds.; Plenum Press: New York, 1982; Vol. 4, pp 79–144.

(5) Ellis, P. D. *Science (Washington, D.C.)* **1983**, *211*, 1141–1145.

(6) Armitage, I. M.; Boulanger, Y. "NMR of Newly Accessible Nuclei"; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, pp 337–365.

(7) Morris, G. A.; Freeman, R. *J. Am. Chem. Soc.* **1979**, *101*, 760–762.

(8) Bendall, M. R.; Pegg, P. T.; Doddrell, D. M. *J. Magn. Reson.* **1981**, *45*, 8–29.

(9) Bax, A.; Niu, C.-H.; Live, D. *J. Am. Chem. Soc.* **1984**, *106*, 1150–1151.

(10) Live, D. H.; Davis, D. G.; Agosta, W. C.; Cowburn, D. *J. Am. Chem. Soc.* **1984**, *106*, 6104–6105.

(11) Müller, L. *J. Am. Chem. Soc.* **1979**, *101*, 4481–4484.

(12) Bendall, M. R.; Pegg, D. T.; Doddrell, D. M. *J. Magn. Reson.* **1983**, *52*, 81–117.

(13) Bodenhausen, G.; Ruben, D. J. *Chem. Phys. Lett.* **1980**, *69*, 185–190.

(14) Redfield, A. G. *Chem. Phys. Lett.* **1983**, *96*, 539–543.

(15) Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301–315.

(14) Dervan, P. B.; Squillacote, M. E.; Lahti, P. M.; Sylwester, A. P.; Roberts, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 1120–1122.

(15) The compound decomposed explosively on one occasion but with insufficient force to break the flask.

(16) Photolysis of these products does not produce a triplet ESR signal.

(17) Light from a 1000-W Xe arc lamp was filtered through water, Pyrex, and Corning CS 1-75 and 7-54 filters (315 ≤ λ ≤ 415 nm; λ ≥ 670 nm). Sensitized photolysis for 1 min produces a nearly photostationary concentration of biradical **1** (Figure 1), which is about 10 times that obtained upon direct photolysis.

(18) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763–1772. de Groot, M. S.; van der Waals, J. H. *Physica* **1963**, *29*, 1128–1132.

(19) Dowd, P.; Gold, A.; Sachdev, K. *J. Am. Chem. Soc.* **1968**, *90*, 2715–2716. Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242–248.