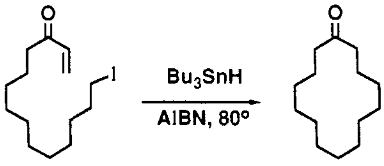
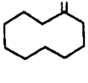
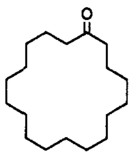
reagents. With the bromide **1b**, the best yields of cyclotetradecanone[19] we could achieve under any conditions tried was 35% and yields in the 20–30% range were typical. The simple expedient of working with the iodide rather than the bromide raised the yields to 60–65% for **1c**, presumably because of better propagation at the alkyl iodide–stannyl radical step.[20] The conditions which we have found to be most convenient for radical macrocyclization are as follows: The iodide (3–6 mM) in dry benzene, along with 1.1 equiv of tributyltin hydride and 0.1 equiv of the initiator AIBN is refluxed for 3 h under argon. Solvent removal and chromatography on silica eliminate tin products providing the cycloalkanone and acyclic reduction product (**1e–g**) mixture.[21] The cycloalkanones **7–11**[18] could be prepared by this procedure, and the yields of macrocyclization along with reduction are presented in Table I.



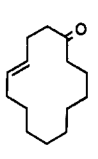
1c 7, 65%



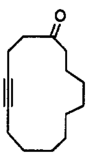
8



9



10



11

Reactions carried out at higher concentrations of substrate and tin hydride gave considerably more acyclic products and generally lower overall product yield than reactions carried out at 3–6 mM substrate. The increase in acyclic to cyclic products at higher concentrations results from more favorable competitive H-atom transfer to the acyclic radical and the decrease in recovery under these conditions probably results from competitive addition of the acyclic radical in an intermolecular event. We note that such intermolecular reactions have a kinetic advantage at substrate concentrations greater than 10 mM in S_N2 macrolactonization systems.[12,24]

A series of quantitative experiments for the substrate **1c** was carried out at 80 °C in benzene and a rate ratio of cyclization to H-atom transfer for the acyclic radical was determined, $k_c/k_H = 2 \times 10^{-3}$ M^{-1}. On the basis of the known k_H for H-atom transfer from tributyltin hydride to primary alkyl radicals of 6.2×10^6 M^{-1} s^{-1},[25] the rate constant k_c for the radical derived from **1c** is 1.2×10^4 s^{-1}.

Particular comment should be made about the substrates **2a** and **3a**. These systems lead to higher yields of macrocycles than the fully saturated substrates, in some cases the product accountability being nearly quantitative. For both of these substrates, the possibility of serial cyclization is an issue, since the radical generated by addition to the α,β-unsaturated ketone has the possibility of a second transannular 5-exo cyclization. We have been unable to detect such serial cyclization products (**3a** would give a [9.3.0] system, for example), but we are continuing to examine this possibility for other substrates.

The construction of macrocyclic systems is a long-standing problem in synthetic organic chemistry.[26] Substituted macrocyclic ketones and lactones would appear to be available without elaborate protection–deprotection schemes by the method described here. In this regard, we have carried out preliminary experiments that confirm that the method can be extended to macrolide systems, intramolecular radical addition to acrylate esters providing the lactone by C–C bond formation.

Acknowledgment. NAP gratefully acknowledges support of this research from NIH (HL-17921).

---

[19] We thank Professor J. Marshall and V. Audia of the University of South Carolina for an authentic sample of cyclotetradecanone.

[20] Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343.

[21] Medium-pressure chromatography is generally required to separate the cycloakanone from the reduction product.

[22] We thank Drs. H. Bost and J. Byers of Bartelsville, OK, for an authentic sample of cycloocatadecanone.

[23] A complete kinetics study of the systems reported here will be subsequently published.

[24] We have isolated two products from **1a**–tin hydride reactions which preliminary data suggest are dimer-type products.

[25] Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739. An iterative procedure developed by Professor M. Newcomb of Texas A&M gives $k_c = 3.9 \times 10^4$ s^{-1}. We thank Dr. Newcomb for helpful discussions.

[26] Masamune, S.; Bates, G. S.; Corcoran, J. W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 585.

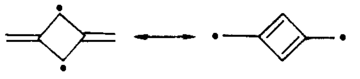
Dimethylenecyclobutadiene

Paul Dowd* and Yi Hyon Paik

Department of Chemistry, University of Pittsburgh
Pittsburgh, Pennsylvania 15260

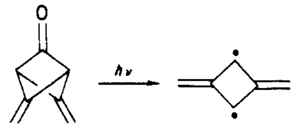
Received September 25, 1985

Dimethylenecyclobutadiene (I) may be considered to be an edge-to-edge, double trimethylenemethane[1,2] or a cyclobutadienyl dicarbinyl diradical. From a broader perspective, the diradical I is a new member of the non-Kekulé class of molecules;[3] it is also a new six-π-electron isomer of benzene. Dimethylenecyclobutadiene (I) is predicted to be a ground-state triplet.[4] For these reasons, there is substantial incentive to synthesize I, to explore its spectroscopic properties,[5] and to examine its chemical reactivity.



I

Our approach to I was predicated upon low-temperature photolytic excision of carbon monoxide from the ketone dimethylenebicyclo[1.1.1]pentanone (II).[6]



II I

Direct irradiation of the ketone II at 260 nm in the cavity of a Varian E-4 ESR spectrometer at 10 K yielded the triplet spectrum shown in Figure 1.[7] The spectrum is characterized by

---

[1] Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587.

[2] Reviews: Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. Berson, J. A. *Ibid.* **1978**, *11*, 446. Berson, J. A. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; p 151.

[3] The non-Kekulé appelation is due to: Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969; pp 232–234. The first non-Kekulé compound to be observed by ESR was trimethylenemethane.[1]

[4] Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587. Davidson, E. R.; Borden, W. T.; Smith, J. *Ibid.* **1978**, *100*, 3299, and references therein.

[5] See the recent observation of I by: Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774. Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1986**, *108*, 299.

[6] The ketone II was synthesized from 3,4-diazatetracyclo[4.3.0.0^{1,7}.0^{6,9}]nonan-8-one by oxidative extrusion of nitrogen.

[7] There appears to be no dependence on the matrix; the same spectrum was observed in methyltetrahydrofuran, isopentane, methylcyclohexane, perfluorobutyltetrahydrofuran (PFBTHF), 1:1 PFBTHF/perfluoroheptane, and 1:1 PFBTHF/perfluorotributylamine.

0002-7863/86/1508-2788$01.50/0

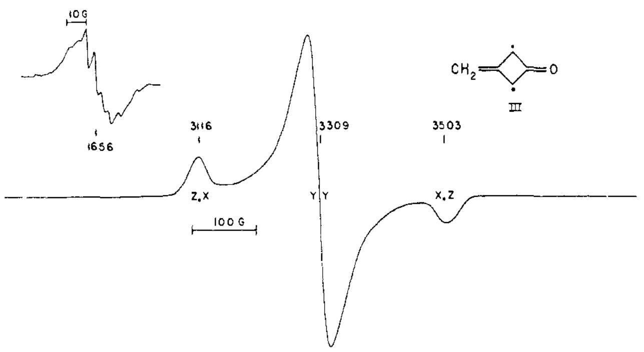


Figure 1. Electron spin resonance spectrum of the 3-methylenecyclobutanone diradical (III) following direct irradiation of the ketone II at 10 K.

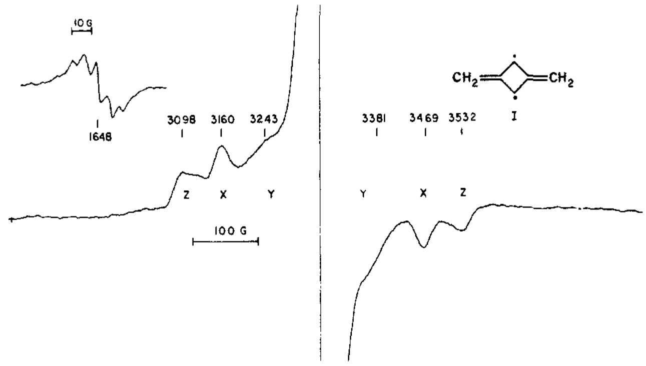
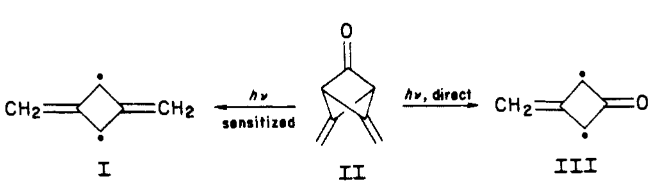


Figure 2. Electron spin resonance spectrum of dimethylenecyclobutadiene (I) following acetophenone-sensitized photolysis of the ketone II.

three $\Delta m = 1$ lines at 3116, 3309, and 3503 G (microwave frequency, 9.26 GHz) and by a $\Delta m = 2$ line at 1656 G (Figure 1, inset). This spectrum is clearly that of a triplet-state molecule, but it is decidedly different from that assigned to the dimethylenecyclobutadiene (I) derived from photolysis of a diazene precursor.[5] The spectrum of Figure 1 is best fit to a spin Hamiltonian with zero field splitting parameters $|D|/hc = 0.018$ and $|E|/hc = 0.006$ cm^{-1}. The large E/D ratio gives the spectrum its unusual three-line appearance. Instead of the typical six-line set of x, y, and z doublets, the large E/D ratio leads to a splitting of the x and y lines such that, as indicated in the spectrum of Figure 1, the x and z lines overlap and the y line is moved to the center of the spectrum. Since the center line is more intense than is appropriate for the two y lines, the spectrum must also consist of monoradical impurities generated in the course of the photolysis. The abnormally large E/D ratio may provide an important clue to the structure of this triplet molecule.

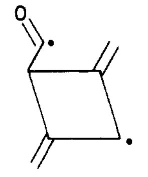
A different result is obtained when the ketone II at 10 K is irradiated at 275 nm in the presence of acetophenone as sensitizer. The triplet spectrum shown in Figure 2 is entirely distinct from that shown in Figure 1 and, with the exception of the monoradical impurity at the center of the spectrum, it is identical with that reported[5] for dimethylenecyclobutadiene. Thus, this spectrum is characterized by $|D|/hc = 0.020$ and $|E|/hc = 0.003$ cm^{-1} with $\Delta m = 1$ lines at 3098, 3160, 3243, 3381, 3469, and 3532 G and with a $\Delta m = 2$ line at 1648 G (microwave frequency, 9.25 GHz).[8]

The product of sensitized photolysis may confidently be identified as dimethylenecyclobutadiene (I) since the same triplet ESR spectrum has now been obtained from independent ketone and azo[5] precursors. The structure of the triplet from direct photolysis may, at this juncture, only be speculated upon. We suggest, as a strictly tentative hypothesis, that this new triplet might be the 3-methylenecyclobutanone diradical (III). This supposition is based upon several considerations: (i) The similarity in the D values of I and III to each other and to that of trimethylenemethane[1] argues that III is a 1,3-diradical, the D value being a sensitive indicator of the extent of interaction between the unpaired electrons. (ii) The electronegative oxygen in the triplet III would polarize the electron distribution in III, and this could lead to the large E/D ratio. In triplet molecules the z line is found at D, the x line at $D + 3E/2$, and the y line at $D - 3E/2$.[9] Accordingly, when E is approximately equal to $D/3$ the x line will move out to overlap with the z line and the y line will move to the center of the spectrum. This would account for the three-line spectrum observed in Figure 1 and make the oxygen-substituted triplet III a candidate structure. This analysis also nicely rationalizes the three-line spectrum of m-quinomethane ($D = 0.0266$ and $E = 0.0074$ cm^{-1}) reported by Berson et al.[10] In striking contrast to the latter, the hydrocarbon diradical m-xylylene ($D = 0.011$ and $E \leq 0.001$ cm^{-1}) reported by Platz[11] shows a the normal six-line spectrum. These two examples provide an important parallel with the spectra of the triplets I and III. As a general proposition, it now appears likely that non-Kekulé diradicals asymmetrically substituted with heteroatoms will be characterized by large E/D ratios and three-line spectra such as that of Figure 1.[10b]

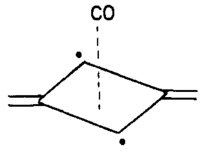


The $\Delta m = 2$ line of the spectrum in Figure 1 (inset) appears to show a nine-line pattern consistent with splitting by two sets of two protons; however, the resolution is not sufficiently satisfactory to warrant a firm structural conclusion at this point. This important structural indicator must await improvements in instrumentation.

Although we think they are unlikely candidates, we cannot strictly rule out structures such as IV and V, where IV is the diradical resulting from cleavage of one bond and V represents a matrix-bound complex between carbon monoxide and dimethylenecyclobutadiene. The diradicals IV and V should be unstable and be converted thermally to I. The triplet ESR spectrum of Figure 1 disappears irreversibly on warming to 60 K, while the spectrum of I persists up to ca. 90 K. Thus, there appears to be no thermal connection between the two spectra as might have been expected if either IV or V were the observed triplet diradical of Figure 1.



IV



V

On the negative side, it is not attractive to be required to break bonds to vinyl carbons to generate III, but this double cleavage does seem to be within reach energetically.[12] In addition, although

---

[8] The low intensity z lines of III could be discerned in most of the spectra of I. This is assumed to arise from an unsensitized component to the photolysis.

[9] See: Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

[10] (a) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787. This paper reports a three-line triplet spectrum for m-quinomethane with $D = 0.0266$ and $E = 0.0074$. In order to obtain a good fit to the spectrum, use was made of an anisotropic g tensor. (b) See also, for another example: Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5146.

[11] (a) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York; p 216. (b) Wright, B. B.; Platz, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 628.

[12] We estimate (MM2) the ΔH_f of II to be 93.6 kcal/mol and the ΔH_f of the diradical III to be 62.5 kcal/mol. The ΔH_f of vinylidene carbene (CH_2=C:) has been estimated to be 98 kcal/mol.[14] Thus, approximately 70 kcal/mol is required for cleavage, a value well below the 110 kcal/einstein available from light of wavelength 260 nm. We thank David Spellmeyer for the MM2 calculations.

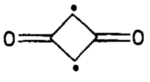
[13] See: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Reading, MA, 1978; p 229.

[14] Kirshnan, R.; Frisch, M. J.; Pople, J. A.; Schleyer, P. v. R. *Chem. Phys. Lett.* **1981**, *79*, 408.

the parallel between *m*-quinomethane and *m*-xylylene and the spectra of Figures 1 and 2 is illuminating, it should also be noted that the effect of the oxygen in *m*-quinomethane makes the D value (0.0266 cm^{-1}) about twice as large as that of *m*-xylylene (0.011 cm^{-1}).[16] The same trend is not observed in the spectra of Figures 1 and 2 as might have been expected if III were the correct structure corresponding to the triplet of Figure 1. At the same time an accurate assessment of D values is unfortunately not at hand so this point cannot now be decided with finality.

It is attractive to hypothesize that the product of α-cleavage, dimethylenecyclobutadiene (I), is a consequence of n $\rightarrow$ π^* excitation while the diradical III arises by β-cleavage from a $\pi \rightarrow \pi^*$ excited state; both cleavage reactions would then be under stereoelectronic control.[13]

Curie law plots of the intensities of the $\Delta m = 2$ lines vs. $1/T$ lead to the conclusion that both I and III are ground-state triplets. This is intriguing because the next member of the series, the 1,3-cyclobutanedione diradical (VI), has been predicted to be a ground-state singlet.[15]



VI

Acknowledgment. We thank Philip Garner and Raymond Schappert for early exploratory studies, Celia Go for preparing starting materials, and, particularly, Professor David W. Pratt for helpful discussions and assistance with the ESR measurements. This research was generously supported by the National Science Foundation. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial suport of this research.

---

(15) Gleiter, R.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 214. Schleyer, P. v. R.; Budzelaar, P. H. M.; Cremer, D.; Kraka, E. *Ibid.* **1984**, 23.

(16) Also kindly pointed out by Professors Matthew Platz and Dennis Dougherty.

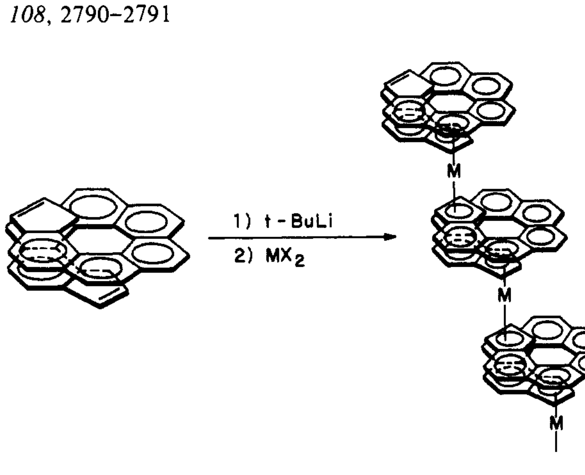
Synthesis of a Helical Metallocene Oligomer

Anantha Sudhakar, Thomas J. Katz,* and Bing-Wei Yang

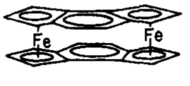
Department of Chemistry, Columbia University
New York, New York 10027

Received August 19, 1985

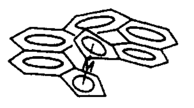
Helicenes that are sufficiently large and capped by unsaturated five-membered rings should yield previously unknown conjugated polymeric metallocenes (eq 1),[1] for, unlike planar hydrocarbons, helicenes cannot form dimers like **3**,[2,3] and they cannot form monomers like **4**[4,5] if their five-membered rings do not superimpose. If the polymeric metallocenes were optically active, their conductive, magnetic, and optical properties might be unusual. We are reporting the synthesis and optical properties of the first, an oligomer with 3–4 units.



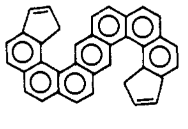
1 **2** (1)



3



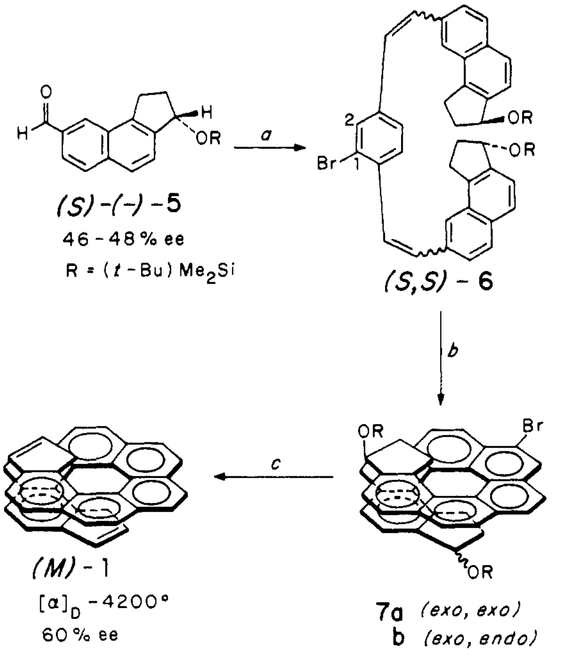
4a (M = Fe)
b (M = Co$^+$PF$_6^-$)



8

The preparation of hydrocarbon **1** (Scheme I) is easy and has three features.[6-9] (1) A bromine directs the photocyclization by blocking both the position it occupies (C-1) and the one adjacent (C-2).[7] In its absence, the cyclization gives only the planar isomer **8**.[7a] (2) Propylene oxide consumes HI generated during photoirradiation, preventing ROH functions from being eliminated prior to cyclization.[5] In its absence, (*R*,*R*)-**6** gives helical product, but

Scheme I



[a] 1,4-*bis*[(C$_6$H$_5$)$_3$P$^+$CH$_2$]-2-Br-C$_6$H$_3$ 2Br$^-$ (0.5 equiv wt),[7] LiOEt (1.1 equiv wt), EtOH, 25 °C, 5–12 h, 95–100% yield.

[b] *hν*, C$_6$H$_6$, I$_2$ (2.2 equiv wt), propylene oxide, 4–12 h.

[c] (1) *t*-BuLi, tetrahydrofuran, −78 °C; (2) H$_2$O; (3) *p*-toluenesulfonic acid, C$_6$H$_6$, 80 °C, 10 min (45–56% yield from **6**).

---

(1) (a) Carraher, C. E., Jr.; Sheats, J. E.; Pittman, C. U., Jr. *Organometallic Polymers*; Academic Press: New York, 1978. (b) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149.

(2) Katz, T. J.; Slusarek, W. *J. Am. Chem. Soc.* **1979**, *101*, 4259.

(3) (a) Katz, T. J.; Schulman, J. *J. Am. Chem. Soc.* **1964**, *86*, 3169. (b) Katz, T. J.; Balogh, V.; Schulman, J. *Ibid.* **1968**, *90*, 734.

(4) (a) Katz, T. J.; Pesti, J. *J. Am. Chem. Soc.* **1982**, *104*, 346. (b) Pesti, J. Ph.D. Dissertation, Columbia University, New York, NY, 1981.

(5) Sudhakar, A.; Katz, T. J. *J. Am. Chem. Soc.* **1986**, *108*, 179.

(6) For (*S*)-(−)-**5**, see ref 5.

(7) (a) Sudhakar, A.; Katz, T. J. *Tetrahedron Lett.*, in press. (b) Contamination by material with skeletal structure **8** is ≤5%.

(8) New compounds exhibited satisfactory NMR, IR, and (except for the salts) mass spectra (including, for key compounds, high-resolution mass spectra). The olefinic and allylic proton resonances of **1** (supplementary material) are shifted, as expected, to higher field than in simpler indenes.[1,4b,5]

(9) Isomers of **6** in which both ether functions are in the other benzylic position do not give appreciable amounts of helical product. When the ethers are in the non-benzylic position the product is helical, but the ethers could not be eliminated.[10]

0002-7863/86/1508-2790$01.50/0