Acknowledgment. We thank Dr. Jean Kossanyi for helpful discussions. The National Science Foundation (Grants CHE 7915228 and CHE 8213637) provided financial support. H.S. thanks the Japan/U.S. Cooperative Photosynthesis and Photoconversion Research Program for financial support. Transient experiments were performed at the Center for Fast Kinetics Research at the University of Texas at Austin, supported by NIH Grant RR-00886 from the Biotechnology Branch of the Division of Research Resources and by the University of Texas. Mass spectral and NMR analyses of **1b** and **1c** were performed respectively on a Hitachi RMU-6MG mass spectrometer at The University of Tsukuba and a Nicolet NT 360 NMR spectrometer at the Research Institute for Polymers and Textiles, Tsukuba.

Registry No. 1a, 1444-65-1; **1b**, 22612-62-0; deuterium, 7782-39-0.

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[20] Wagner and Chiu (Wagner, P. J.; Chiu, C. *J. Am. Chem. Soc.* **1979**, *101*, 7134) have, however, observed a substantially larger isotope effect in one case.

Automerization Mechanism and Structure of the $C_{11}H_{11}$ Armilenyl Cation

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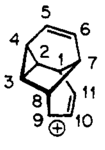
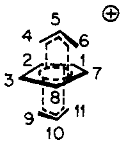
The facile nuclear permutations of the "[3.5.3]armilenyl" cation (**1**)—(1,2,3,8,7)(4,6,9,11)(5,10)—have hitherto obscured any umambiguous structural assignment. The options have been (i) the classical 9-tetracyclo[5.4.0.$0^{2,4}$.$0^{3,8}$]undeca-5,10-dienyl cation (**1a**), (ii) an entirely organic sandwich whose cyclopentadienide ring is spanned in C_2 symmetry by two mutually perpendicular 1,3-dehydroallyl ligands (**1b**), or else (iii) the C_s variant of **1b**, achieved by a mere 9° internal rotation.[1a] The permutations have been analyzed by Longuet–Higgins group theory,[2] and the static structure by EHT[3a] and CNDO calculations.[3b] **1** was the first reported $(CH)_{11}$ cation, and it might yet be the most stable of all;[4] both the cation[1] and its 9-hydroxyl derivative[5] have since been obtained from alcohol, chloride, and ketone precursors that represent as many as five structurally isomeric carbon skeletons.

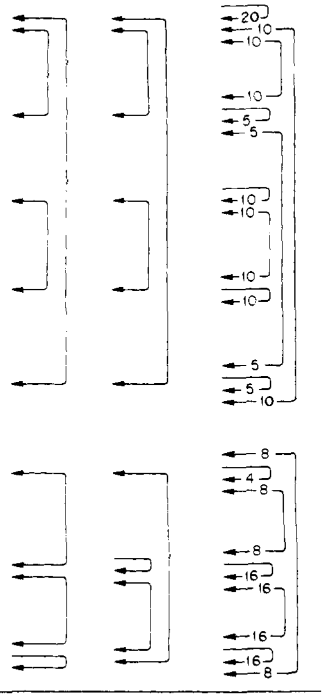


1a



1b

Table I. ^{13}C NMR Assignments of 1a and Alternative Exchange Diagrams for Its Automerization

NMR signal	δ_C[a]	assignment[b]	exchange diagrams of alternative mechanisms[c]: allylic alkylation 1-jump	Wagner-Meerwein 3-jump	sandwich random
a	214.66	9, 11			
b	144.34	6			
c	139.65	5[d]			
d	137.22	10[d]			
e	71.61	4			
f	57.32	7			
g	56.24	1, 8			
h	43.73	2, 3			

[a] 75.47 MHz, −164.1 °C, $FSO_3H/SO_2ClF/SO_2F_2/CHFCl_2/CHF_2Cl$ solution of *anti*-bicyclo[4.3.2]undeca-2,4,6,10-tetraen-9-ol.[1b] [b] Reference 6a. [c] Reference 6b. [d] Alternative c/d assignments are possible but mechanistically irrelevant.

We now report the experimentally required resolution, both of this structural problem and of the mechanistic problem that the correct structure reveals.

Contemporary ^{13}C NMR techniques resolve the previously reported[1a] three lines into eight (Table I). Their number excludes **1b**, and their dispersion excludes its C_s variant. Only **1a** remains.

Figure 1 revives **1b**, albeit now as a potential transient in the automerization of **1a**. Rapid rotation of its cyclopentadienyl ring should randomly generate any of the 20 **1a** label isomers by the radial "sandwich" mechanism. The perimeter of this figure illustrates the originally proposed alternative: the rare allylic alkylation of a cyclopropane ring with inversion of configuration.[7]

The third and final alternative appears in Figure 2. Its exchange diagram (Table I) requires the C1,8 signal to broaden with temperature half as rapidly as the C2,3 signal. The sandwich mechanism requires an equal rate for both signals, whereas the alkylation mechanism requires the first of these signals to broaden twice as rapidly as the second. Figure 3 leaves no doubt but that the last of these mechanisms is most consistent with the data. The associated activation parameters (−160 → −80 °C) are $\Delta H^{\ddagger} = 5.2(1)$ kcal/mol and $\Delta S^{\ddagger} = 0(1)$ cal/(mol deg).

The allylic alkylation mechanism is not merely sufficient to accomodate these data, it is also necessary—at least in the sense

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† Procter and Gamble Co. Fellow, 1981–1982. Taken in part from the Ph.D. Thesis of J.P.D., Cornell University, 1984. Current address: Department of Chemistry, University of Rochester.

[1] (a) Goldstein, M. J.; Kline, S. A. *J. Am. Chem. Soc.*, **1973**, *95*, 935; **1981**, *103*, 2910. (b) Goldstein, M. J.; Tomoda, S.; Pressman, E. J.; Dodd, J. A. *Ibid.* **1981**, *103*, 6530. (c) Fujise, Y.; Yashima, H.; Sato, T.; Itô, S. *Tetrahedron Lett.* **1981**, 1047.

[2] (a) Trindle, C.; Bouman, T. D. *Jerusalem Symp. Quantum Chem. Biochem.* **1973**, *6*, 51. (b) Trindle, C.; Bouman, T. D. *Int. J. Quantum. Chem. Symp.* **1975**, *No. 9*, 255. (c) Trindle, C.: Bouman, T.; Datta, S.; Duncan, C. *Comput. Chem. Res. Educ. Proc. Int. Conf.* **1977**, 261.

[3] (a) Hoffmann, R.; Rossi, A., private communication. (b) Trindle, C.; Hwang, J.-T.; Hough, D. *Tetrahedron* **1974**, *30*, 1393.

[4] The monocyclic isomer has not yet been reported.

[5] (a) Groves, J. T.; Ma, K. W. *Tetrahedron Lett.* **1973**, 5225; (b) *Ibid.* **1975**, 1411. (c) Aumann, R. *Chem. Ber.* **1977**, *110*, 1432.

[6] (a) Carbon assignments derive from peak areas, from the high-temperature δ_C averages (161.33, 138.59, 51.23 ppm), and by analogy with those of the structurally unambiguous *exo*-6-tricyclo[3.3.1.$0^{2,4}$]non-7-enyl cation; Cf. Supplementary Material. (b) The succinct exchange diagram notation of Oth et al. (Oth, J. F. M.; Müller, K.; Gilles, J.-M.; Schröder, G. *Helv. Chim. Acta* **1974**, *5*, 1415) is only trivially extended to accommodate the random process.

[7] Inversion is reported for the electrophilic bromination of cyclopropane (Lambert, J. B.; Schulz, W. J., Jr.; Mueller, P. H.; Kobayashi, K. *J. Am. Chem. Soc.* **1984**, *106*, 793) and for automerizations of the cyclopropylcarbinyl cation (Olah, G. A.; Kelly, D. P.; Jeuel, C. L.; Porter, R. D. *Ibid.* **1970**, *92*, 2544. Majerski, Z.; Schleyer, P. v. R. *Ibid.* **1971**, *93*, 665. Wiberg, K. B.; Szeimies, G. *Ibid.* **1970**, *92*, 571) and *exo*-deltacyclyl cation (Freeman, P. K.; Balls, D. M.; Blazevich, J. N. *Ibid* **1970**, *92*, 2051).

[8] Hoffmann, R. *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

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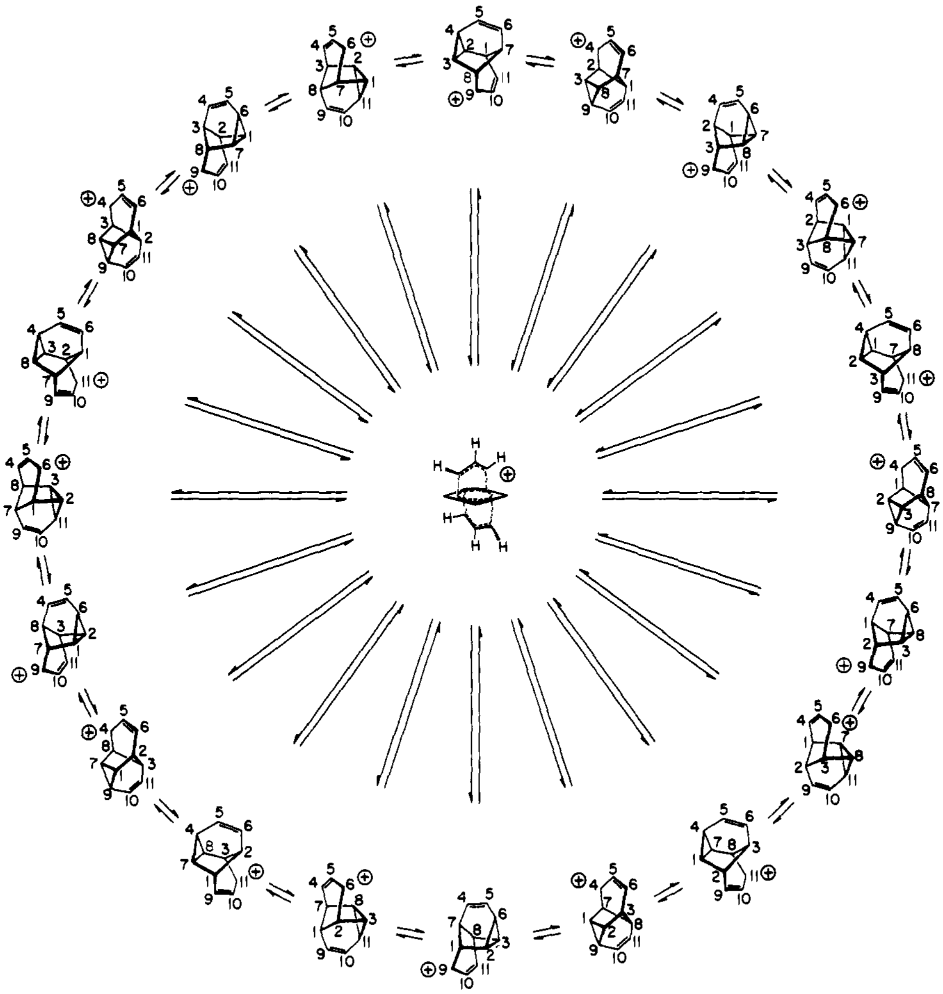

Figure 1. Alternative sandwich and allylic alkylation automerization mechanisms.

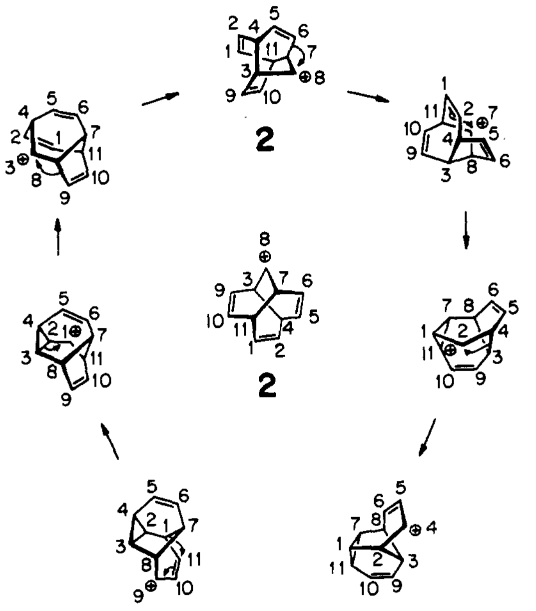

Figure 2. "Wagner-Meerwein" 3-jump mechanism: a Wagner-Meerwein/cyclopropylcarbinyl-homoallyl/Wagner-Meerwein sequence, which is then reflected by the C_2 symmetry of intermediate **2**. As illustrated, it transforms the topmost label isomer of Figure 1 into that which replaces it, when 3/20 of a counter-clockwise rotation operates on that circle. Both the starting isomer and sense of rotation are arbitrary.

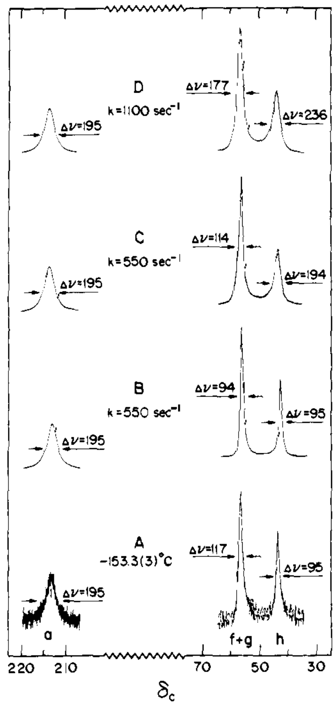

Figure 3. Comparison of the experimental ^{13}C NMR spectrum (A), with those simulated for the 1-jump (B), 3-jump (C), and random (D) alternatives. Each simulation was achieved by fitting only the mechanistically irrelevant a peak width, here expanded to 1.5 times the scale of the others. All $\Delta\nu$ are in hertz. The higher temperature (cf. Table I) sacrifices resolution to achieve symmetrically broadened peaks.

that all other NMR-distinguishable processes have now been excluded. The symmetry of Figure 1 permits each of six possible exchange diagrams to be associated with its own quadruplet of

"$(10 \pm 5 \pm n)$-jump" perimeteral processes; $n = 0 \rightarrow 5$. For example, the "3-jump" process of Figure 2 belongs to $n = 2$, a set that also includes 7-, 13-, and 17-jump processes, all of them now excluded. Four more sets, $n = 0$, 1, 3, and 5, are all incompatible with the high-temperature average spectrum. Within the sole remaining set, $n = 4$, the C_s symmetry of **1a** allows allylic alkylation to be described equally well as 1-jump or 19-jump. Neither these nor any other NMR data, however, can exclude an alternative 9 (or 11)-jump process, nor can they exclude multistep equivalents. The transient carbocations within each equivalents, however, are limited to those that introduce no new elements of structural or permutational symmetry.

The exclusion of **1b**, both as a static structure and as a transient intermediate, now removes the only isolobal[8] metallocene analogue from hydrocarbon chemistry.[9] It will be interesting to see how many other polyhedral carbocations[10] can survive a comparably stringent experimental test.

Acknowledgment. We are grateful to M. Saunders for a copy of his line-shape simulation program and to R. Hoffmann and P. v. R. Schleyer for their early encouragement. Financial support was provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society, as well as by National Science Foundation grants for research (CHE77-26482, CHE82-01052) and NMR instrumentation (CHE-79-04825).

Supplementary Material Available: A -164 °C ^{13}C NMR spectrum and the derivation of its peak assignments (10 pages). Ordering information is given in any current masthead page.

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[9] The 1,3-dehydroallyl cation ligands of **1b** have, however, since reappeared as "open cyclopropenium"cation ligands in organometallic chemistry: Jemmis, E. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2570.

[10] (a) Schwarz, H. *Angew. Chem.* **1981**, *93*, 1046; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 991. (b) Minkin, V. I.; Minyaev, R. M. *Prog. Theor. Org. Chem.* **1982**, *3*, 121.

Visible Light Induced Hydrogen Production from in Situ Generated Colloidal Rhodium-Coated Cadmium Sulfide in Surfactant Vesicles

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Macrodispersed and colloidal semiconductors are utilized increasingly in photochemical solar energy conversion.[1] Band-gap excitation produces an electron-hole pair whose recombination can be intercepted by catalysts, which may, in turn, lead directly to water splitting.[2] However, charge recombination renders such a system inefficient.[3] Separate development of sacrificial oxidation and reduction half-cells and their subsequent coupling, through space or time, provides an alternative approach. Such an approach has been fruitfully employed in homogeneous solutions using organized surfactant assemblies to compartmentalize sensitizers, relays, and catalysts and hence to aid charge separation.[4] The present communication reports the first use of surfactant vesicle-stabilized, in situ formed, catalyst-coated, colloidal semiconductor in artificial photosynthesis. Band-gap excitation by visible light ($\lambda > 350$ nm) of rhodium-coated colloidal cadmium sulfide, in dihexadecylphosphate (DHP) surfactant vesicles, produced hydrogen in the presence of thiophenol.

Preparation and characterization of DHP surfactant vesicles have been described.[5] $CdCl_2$, $RhCl_3$, or methylviologen (MV^{2+}) were incorporated by cosonicating these ions with DHP and then removing externally adsorbed or nonadsorbed cations by cation-exchange chromatography.[6] Entrapment rates of 45–50% $CdCl_2$[7] corresponded to the adsorption of Cd^{2+} on the inner walls of negatively charged DHP vesicles.[8] Exposure of vesicle-entrapped $CdCl_2$ to excess gaseous H_2S resulted in CdS formation. Assuming complete reaction, the absorbance of vesicle-entrapped CdS at 400 nm corresponds to $\epsilon = 1000$ M^{-1} cm^{-1} (Figure 1A). Ultraviolet irradiation with a 450-W xenon lamp under Ar bubbling for 60 min mediated the reduction of Rh^{3+} to Rh^0 in the presence of CdS. Rhodium reduction was monitored by absorption spectroscopy (Figured 1A).

Air-saturated, vesicle-entrapped, colloidal CdS showed the characteristic weak fluorescence emission due, primarily, to electron-hole recombination.[9] Fluorescence intensity maximum (ca. 500 nm)[10] corresponded to full band-gap emission. The fluorescence intensity is strongly reduced in the presence of Rh^{3+} (Figure 1B) and disappears completely after reduction of Rh^{3+} to Rh^0. However, UV irradiation under Ar bubbling in the absence of Rh^{3+} does not affect the intensity of CdS fluorescence. Quenching of CdS fluorescence by coentrapped Rh^{3+} appears to be Stern-Volmer as a function of the initial concentraion of Rh^{3+} (Figure 2).[11] Coentrapped MV^{2+} strongly quenches CdS fluorescence and deviates from a Stern-Volmer quenching, indicating the possibility of a static quenching (Figure 2). Interestingly, externally adsorbed MV^{2+} does not quench vesicle-entrapped CdS fluorescence, even several days after being added to CdS-containing vesicles. This is consistent, with the CdS being located completely inside of the vesicles and with neither MV^{2+} nor CdS leaking through the DHP vesicles under the present experimental conditions. Thiophenol, PhSH, also quenches the fluorescence of reversed micelle-entrapped CdS fluorescence.[12]

The hydrodynamic radius of the vesicles, after CdS formation, was found to be 550 ± 50 Å.[13] Vesicle sizes were not affected

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[1] Grätzel, M. *Acc. Chem. Res.* **1981**, *14*, 376. Darwent, J. R.; Porter, G. *J. Chem. Soc., Chem. Commun.* **1981**, 145. Darwent, J. R. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1703. Kalyanasundaran, K.; Borgarello, E.; Grätzel, M. *Helv. Chim, Acta.* **1981**, *64*, 362.

[2] Borgarello, E.; Kiwi, J.; Pelizetti, E.; Visca, M.; Grätzel, M. *J. Am. Chem. Soc.* **1981**, *103*, 6324.

[3] Bard, A. J. *J. Phys. Chem.* **1982**, *86*, 172.

[4] Fendler, J. H. "Membrane Mimetic Chemistry"; Wiley-Interscience: New York, 1982.

[5] Lee, L. Y.; Hurst, J. K.; Politi, M.; Kurihara, K.; Fendler, J. H. *J. Am. Chem. Soc.* **1982**, *105*, 370.

[6] Typically 49.2 mg of DHP were sonicated in 30 mL of triply distilled water to give stoichiometric concentrations of 3.0×10^{-3} M DHP, 3×10^{-4} M $CdCl_2$, and 1.0×10^{-4} M $RhCl_3$ at pH 7 (with 3.0×10^{-3} M NaOH during sonication). Under the present experimental conditions, essentially all cations (Cd^{2+} and Rh^{3+}) were adsorbed on either side of the vesicles. After cation-exchange chromatography, 45–50% of the initial amount of Cd^{2+} was retained inside of the vesicles,[7] which corresponded to the fraction of Cd^{2+} adsorbed on the inner walls of negatively charged DHP vesicles.[8] Entrapment rates in the absence of adsorption would be controlled by the inner volume fraction, which is approximately 0.5% of the total volume of the vesicle dispersion. The amount of Cd^{2+} ions entrapped in a single vesicle is proportional to the number of DHP surfactants forming the inside layer. As these vesicles have a rather broad size distribution,[8] this will be reflected on the sizes of CdS particles formed inside of the vesicles. Typically, for an aggregation number of 50000 DHP surfactants per vesicle, approximately 22000 surfactant molecules will form the inside layer, entrapping by adsorption 2200 Cd^{2+} ions under the present experimental conditions and the same amount of CdS molecules will be produced in such a vesicle after exposure to H_2S. It is believed that these CdS molecules eventually agglomerate in one single particle per vesicle. However, no trace of CdS precipitation is observed after several weeks, thus indicating the efficiency of the DHP vesicles to stabilize the colloidal CdS dispersion.

[7] Determined by atomic absorption spectroscopy.

[8] Tricot, Y.-M.; Furlong, D. N.; Sasse, W. H. F.; Daivis, P.; Snook, I.; Van, Megen, W. *J. Colloid Interface Sci.* **1984**, *97*, 380.

[9] Duonghong, D.; Ramsden, J.; Grätzel, M. *J. Am. Chem. Soc.* **1982**, *104*, 2977. Henglein, A. *J. Phys. Chem.* **1982**, *86*, 2291. Kuczyuski, J. P.; Milosavljevic, B. H.; Thomas, J. K. *Ibid.* **1983**, *87*, 3368. Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 301.

[10] No correction was made for the photomultiplier response.

[11] Concentrations of Rh^{3+} shown in Figure 2 refer to those added initially, since the amounts entrapped were not directly determined. Entrapment rates of Rh^{3+}, by analogy with Cd^{2+} and other adsorbates,[8] are assumed to be 45–50%.

[12] Meyer, M.; Wallberg, C.; Kurihara, K.; Fendler, J. H. *J. Chem. Soc., Chem. Commun.* **1984**, 90.

[13] A Malvern 2000 light-scattering system and a Spectra Physics 171 Ar^+ laser were used. Data were collected at $\theta = 90°$, at 23 °C. *Q* values (polydispersities) were in the order of 0.3.

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