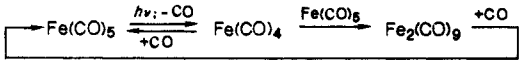
process is quantitative [first-order $k = (2.8 \pm 0.1) \times 10^{-6}$ s^{-1} at 27 °C; this ordinarily requires high CO pressures[22]], demonstrating that even the small CO molecules are trapped next to $Fe_2(CO)_9$ within microcavities in the host. Scanning electron microscope (150000×) reveals $Fe(CO)_5$ and $W(CO)_6$ salted in KBr as dimensionless dots imaging as the respective metal; these guest aggregates are at most 10 Å in diameter.

Single-molecule isolation is an important goal. We have succeeded in isolating salted $Fe(CO)_5$ using a three-component system. Codeposition of $Fe(CO)_5$, an alkane (*n*-pentane, isopentane, neopentane, cyclopentane, or 3-methylpentane), and KBr (1:10:2000) yielded a material with sharp IR bands of $Fe(CO)_5$ (Figure 1). After a time amply sufficient to convert $Fe(CO)_5$ salted in KBr to $Fe_2(CO)_9$ + CO, room-temperature UV irradiation of $Fe(CO)_5$ cosalted with an alkane in KBr had no effect. Extended irradiation eventually destroyed all carbonyl IR bands, but even then, no $Fe_2(CO)_9$ was detected.

We propose that the ternary material contains $Fe(CO)_5$ molecules mutually isolated within alkane-filled microcavities in the host. Indeed, while irradiation (308 nm) at 20 K rapidly converts the binary composite to $Fe_2(CO)_9$ and then slowly to $Fe_2(CO)_8$,[23] it converts the ternary material to CO and the C_{3v} form of $Fe(CO)_4$ (Figure 1). This is the stable form of $Fe(CO)_4$ when stabilized by a weak ligand in the fifth coordinating position,[21] perhaps best viewed as $Fe(CO_4)X$ (X = alkane or Br$^-$). Upon warmup, $Fe(CO)_5$ is reformed quantitatively. Thus, the photochemistry of salted $Fe(CO)_5$ can be summarized as follows:



Acknowledgment. This work was supported by the U.S. Army Research Office through Contract DAAG 2984-K-0090.

(22) Dewar, J.; Jones, H. O. *Proc. R. Soc. London, A* **1907**, *79*, 66.
(23) Irradiation of argon matrix isolated $Fe_2(CO)_9$ yields $Fe_2(CO)_8$: Poliakoff, M.; Turner, J. J. *J. Chem. Soc.* **1971**, 2403.

A Comment on the Recently Proposed Mechanism for the Oxidation of Olefins with $PdCl(NO_2)(CH_3CN)_2$

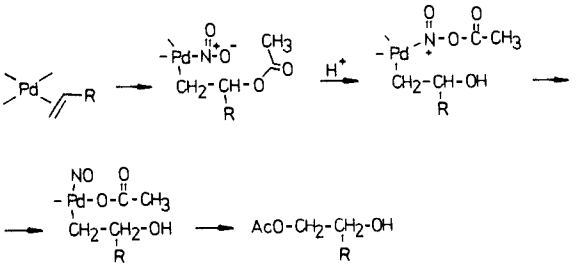
Jan-E. Bäckvall*[1a] and Andreas Heumann*[1b]

Department of Organic Chemistry, Royal Institute of Technology, S-100 44 Stockholm, Sweden
I.P.S.O.I., Faculté des Sciences, Saint Jérôme
L.A. 126 du CNRS, Université d'Aix Marseille III
F-13 013 Marseille, France

Received May 7, 1986

Oxidation of olefins using nitro complexes of palladium(II) has recently attracted attention.[2-4] Depending on the reaction conditions, $Pd(Cl)(NO_2)(CH_3CN)_2$ has been reported to selectively catalyze the oxygen oxidation of olefins to either epoxides, ketones, or glycol monoacetates.[2-4] Mares and co-workers[4] recently reported that oxidation of terminal olefins by $Pd(Cl)(NO_2)(CH_3CN)_2$ (catalytic or stoichiometric) in acetic acid afforded approximately equal amounts of 2-acetoxy-1-alkanol and 1-acetoxy-2-alkanol as the main products. Furthermore, when the nitro group was labeled with ^{18}O, the ^{18}O label was exclusively in the acetate group of the products. To account for these results they suggested a mechanism via an acetoxypalladation, followed by an acetyl migration to an oxygen in the coordinated NO_2 group

Scheme I. Mares's Mechanism[4]



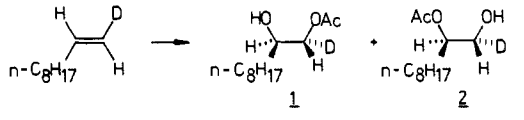
and subsequent acetoxy migration to palladium and reductive elimination (Scheme I).

There are two features with the mechanism proposed by Mares that to us seemed inconsistent with known palladium chemistry. First, the mechanism would require an approximate 1:1 ratio of Markovnikov and anti-Markovnikov acetoxypalladation. Under the conditions used, however, one would expect a high regioselectivity for acetate attack at the nonterminal carbon in the π-olefin complex, in accordance with known acetoxypalladation and oxypalladation reactions.[5,6]

Second, the mechanism would require a reductive elimination between an alkyl group and an oxygen nucleophile. There are hitherto no known examples of such reductive eliminations in palladium chemistry, and a recent ab initio ECP calculation suggests that such a process is highly unlikely due to the low orbital energy of the palladium–oxygen bond.[7] We therefore decided to study the mechanism of this glycol monoacetate process.

Acetoxypalladation of olefins is known[8] to occur with trans stereochemistry across the double bond. Since the mechanism suggested by Mares[4] requires the palladium–carbon bond to be cleaved with retention of configuration at carbon, the result would be an overall trans addition of OH and AcO across the double bond. A simple way of testing Mares's mechanism would therefore be to study the stereochemistry of the glycol monoacetate formation from the olefin.

Reaction of a 2-fold excess of (*E*)-1-deuterio-1-decene[9] with $Pd(Cl)(NO_2)(CH_3CN)_2$[10] in acetic acid under air atmosphere for 2 h[11] afforded **1** and **2** in approximately equal amounts according to GLC, HPLC, and ^1H NMR. Small amounts of 2-decanone

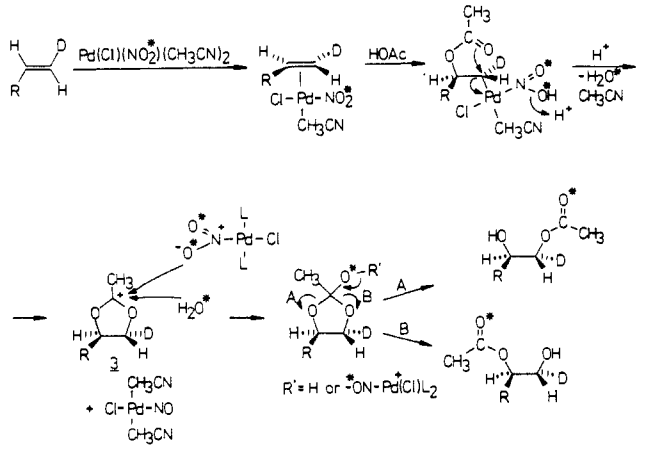


were also formed, the ratio 2-decanone to glycol monoacetate being 1:4 according to GLC. Separation of the glycol monoacetates **1** and **2** by preparative HPLC (silica, hexane/ethyl acetate =

(1) (a) Royal Institute of Technology, Stockholm. (b) Université d'Aix Marseille.
(2) (a) Andrews, M. A.; Kelly, K. P. *J. Am. Chem. Soc.* **1981**, *103*, 2894. (b) Andrews, M. A.; Cheng, C. W. F. *Ibid.* **1982**, *104*, 4268. (c) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F. *Organometallics* **1985**, *4*, 268.
(3) Heumann, A.; Chauvet, F.; Waegell, B. *Tetrahedron Lett.* **1982**, *23*, 2767.
(4) Mares, F.; Diamond, S. E.; Regina, F. J.; Solar, J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3545.
(5) Henry, P. M. *Palladium-Catalyzed Oxidation of Hydrocarbons*; D. Reidel: Dordrecht, 1980.
(6) The anti-Markovnikov acetoxypalladation of terminal olefins only seems to take place at increased acetate concentration and in the absence of chloride ligands: Winstein, S.; McCaskie, J.; Lee, H. B.; Henry, P. M. *J. Am. Chem. Soc.* **1976**, *98*, 6913.
(7) Bäckvall, J. E.; Björkman, E. E.; Petterson, L.; Siegbahn, P. *J. Am. Chem. Soc.* **1985**, *107*, 7265.
(8) (a) Henry, P. M.; Ward, G. A. *J. Am. Chem. Soc.* **1971**, *93*, 1494. (b) Andell, O. S.; Bäckvall, J. E. *J. Organomet. Chem.* **1983**, *244*, 401. (c) Also the results of other studies require a trans acetoxypalladation. For example, the Pd(II)-catalyzed cis acetoxychlorination of specifically deuterated 1-decene[8d] requires a trans acetoxypalladation since later studies (cf. ref 15 and 16) have unambigously shown that the palladium–carbon bond is cleaved with inversion by chloride. (d) Bäckvall, J. E. *Tetrahedron Lett.* **1977**, 467.
(9) Prepared by hydroalumination[9a] followed by D_2O quenching.[9b] The 1-decene-d_1 obtained in this way was completely of *E* stereochemistry (>99% *E*) according to ^1H NMR. (a) Wilke, G.; Müller, H. *Justus Liebigs Ann. Chem.* **1958**, *618*, 267. (b) Patrick, D. W.; Truesdale, L. K.; Biller, S. A.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2628.
(10) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F.; Emge, T. J.; Kelly, K. P.; Koetzle, T. F. *J. Am. Chem. Soc.* **1984**, *106*, 5913.
(11) The conversion of 1-decene-d_1 was complete after this reaction time and the isolated yield of 1-decene-d_1 glycol monoacetates was approximately 60% based on the olefin.

0002-7863/86/1508-7107$01.50/0

Scheme II



70/30) and subsequent ^{1}H NMR analysis showed that **1** and **2** are mainly of the threo configuration, the threo/erythro ratio being 88:12 in both cases. The configuration of **1** and **2** was established by ^{1}H NMR[12] and confirmed by hydrolysis to the diol, of which an independent sample of the erythro isomer was prepared.[13]

Since isomerization of olefin could be responsible for the loss of stereospecificity, the reaction was repeated with a 4-fold excess of (*E*)-1-deuterio-1-decene and was run for only 1 h. This led to only a slight improvement of the threo/erythro ratio to 91:9 (for both **1** and **2**), suggesting that isomerization of the olefin cannot account for all of the loss of stereospecificity. In accordance, ^{1}H NMR analysis of the recovered 1-deuterio-1-decene showed an *E*/*Z* ratio of 94:6. With a change of the *E*/*Z* ratio from 100:0 to 94:6 during the course of the reaction, we conclude that isomerization of the olefin can account for approximately one-third of the erythro isomer found in both cases.

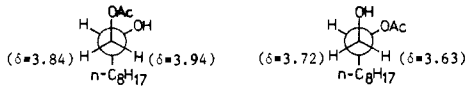
The stereochemical results for the oxidation of 1-deuterio-1-decene with $Pd(Cl)(NO_2)(CH_3CN)_2$[14] require that the palladium–carbon bond is cleaved with >94% inversion of configuration at carbon, and hence the mechanism suggested by Mares[4] cannot be correct. To account for both the stereochemical and labeling experiments, we suggest a mechanism via an acetoxonium intermediate (Scheme II). Trans acetoxypalladation followed by an oxidative cleavage of the palladium–carbon bond with inversion,[15] via neighboring group attack,[16] would give the five-membered cyclic cationic intermediate **3**. In this process, labeled water is generated.[17] The labeled water, or alternatively a coordinated O-labeled nitro group, may now attack the cyclic cationic intermediate at the carbonyl carbon followed by rearrangement to either **1** or **2**. This would explain the 1:1 ratio between **1** and **2**.[18] The 2-decanone can be formed either by the same mechanism as given by Mares[4] or via a Wacker reaction by the water released.

A related mechanism to that proposed here was suggested by Yermakov and co-workers[19] to account for the ^{17}O label in the carbonyl group of ethylene glycol monoacetate obtained from oxidation of ethene by $LiN^{17}O_3/Pd(OAc)_2$ in acetic acid. It is interesting to note that the mechanism proposed in Scheme II has similarities with the mechanism of the "wet" Prevost reaction for preparation of glycol monoacetate from olefins with overall cis addition using bromine and silver acetate in acetic acid.[20]

We conclude that the mechanism proposed here is consistent with stereochemical data, labeling studies, and the regiochemistry observed. In the oxidation of internal olefins to glycol monoacetates by the system $O_2/Pd^{II}/LiNO_3/LiCl$ in acetic acid, an overall cis addition of OH and OAc has been reported.[21] However, the addition to terminal olefins was regioselective and a different mechanism to that reported here is probably operating.

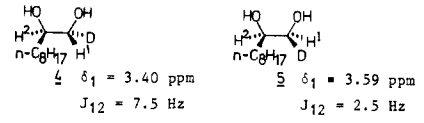
Acknowledgment. We thank the Swedish Natural Science Research Council and CNRS for financial support.

(12) The ^{1}H NMR spectra of the undeuterated parent compounds: **1-acetoxy-2-decanol** ($CDCl_3$) δ 4.14 (dd, J = 11.0, 2.7 Hz, 1 H, CH_2OAc), 3.94 (dd, J = 11.0, 7.4 Hz, 1 H, CH_2OAc), 3.84 (m, 1 H, $CHOH$), 2.10 (s, 3 H, OAc), 1.46 (m, 2 H), 1.28 (m, 12 H), 0.88 (br t, 3 H); **2-acetoxy-1-decanol** ($CDCl_3$) δ 4.91 (m, 1 H, $CHOAc$), 3.72 (dd, J = 12.0, 2.9 Hz, 1 H, CH_2OH), 3.63 (dd, J = 12.0, 6.2 Hz, 1 H, CH_2OH), 2.09 (s, 3 H, OAc), 1.58 (m, 2 H), 1.28 (m, 12 H), 0.88 (br t, 3 H). Since gauche conformations between the hydroxy and acetoxy groups are preferred, the following assingments of the terminal diastereotopic methylene protons can be made:



The product **1** showed a doublet (J = 7.6 Hz) at δ 3.94 and the product **2** showed a broad doublet (J = 6.3 Hz) at δ 3.61.

(13) Hydrolysis of **1** and **2** (NaOH, EtOH-H_2O) in both cases gave *threo*-1-deuterio-1-decane-1,2-diol (**4**). A reference sample of the erythro isomer **5** was prepared by epoxidation of (*E*)-1-deuterio-1-decene and subsequent acid-catalyzed ring opening in aqueous THF. The ^{1}H NMR ($CDCl_3$ + D_2O) spectra of **4** and **5** are different.



(14) The analogous oxidation in the presence of LiOAc according to Mares[4] gave the same stereochemical result but with a slightly higher stereospecificity (threo:erythro = 95:5).

(15) Bäckvall, J. E. *Acc. Chem. Res.* **1983**, *16*, 335.

(16) Bäckvall, J. E.; Nordberg, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 393.

(17) Previous studies show that the labeled water would not exchange significantly with acetic acid under the reaction conditions. Oxygen atom exchange of acetic acid with water is slow and requires the presence of strong mineral acids to occur at a reasonable rate: Bentley, R. *J. Am. Chem. Soc.* **1949**, *71*, 2765. Llewellyn, D. R.; O'Connor, C. *J. Chem. Soc.* **1964**, 545. O'Connor, C.; Turney, T. A. *J. Chem. Soc. B* **1966**, 1211.

(18) The mechanism in Scheme II would seem to give ≤100% yield of oxidation products based on palladium, which is at variance with experimental results.[4] However, the final $PdCl(NO)(CH_3CN)_2$ may continue to react to give Wacker-type oxidation products and Pd(O).

(19) Kuznetsova, N. I.; Likholobov, V. A.; Fedotov, M. A.; Yermakov, Y. I. *J. Chem. Soc., Chem. Commun.* **1982**, 973.

(20) Wiberg, K. B.; Saegebarth, K. A. *J. Am. Chem. Soc.* **1957**, *79*, 6256.

(21) (a) Yoshimura, N.; Tamura, M. *Abstr. Int. Conf. Organomet. Chem., 8th* Kyoto, Japan, 1977; 3Co7, p. 251. (b) Yoshimura, N. *Jpn. Kokai Tokkyo Kono* 76 08, 210; *Chem. Abstr.* **1976**, *85*, 32441r. (c) Tamura, M.; Yasui, T. *J. Chem. Soc. D* **1968**, 1209.

Identification of the Altered Pyrrole in Sulfmyoglobin and an Extractable "Sulfhemin": Participation of the 4-Vinyl Group in the Saturation of the Pyrrole in One Form of Sulfmyoglobin

Mariann J. Chatfield, Gerd N. La Mar,*
Juliette T. J. Lecomte, Alan L. Balch, Kevin M. Smith, and Kevin C. Langry

Department of Chemistry, University of California Davis, California 95616

Received May 9, 1986

The sulfglobins are nonfunctional forms of either myoglobin or hemoglobin where the sequential reaction of the reduced proteins with an oxidizing agent and thiol leads to the formation of a green pigment.[1] The optical spectra have indicated the reduction of a pyrrole to yield a chlorin-type macrocycle which ^{35}S tracer work has shown to contain one atom of sulfur per heme, frequently envisaged as an episulfide across the pyrrole β positions.[2] To date neither the identity of the modified ring nor the chemical nature of the reacted site(s) has been elucidated. While recent spectroscopic studies aimed at elucidating the structure of SMb agree on evidence of a strongly perturbed tetrapyrrole, there is

(1) Berzofsky, J. A.; Peisach, J.; Blumberg, W. E. *J. Biol. Chem.* **1971**, *246*, 3367-3377.

(2) Berzofsky, J. A.; Peisach, J.; Horecker, B. L. *J. Biol. Chem.* **1972**, *247*, 3783-3791.

0002-7863/86/1508-7108$01.50/0