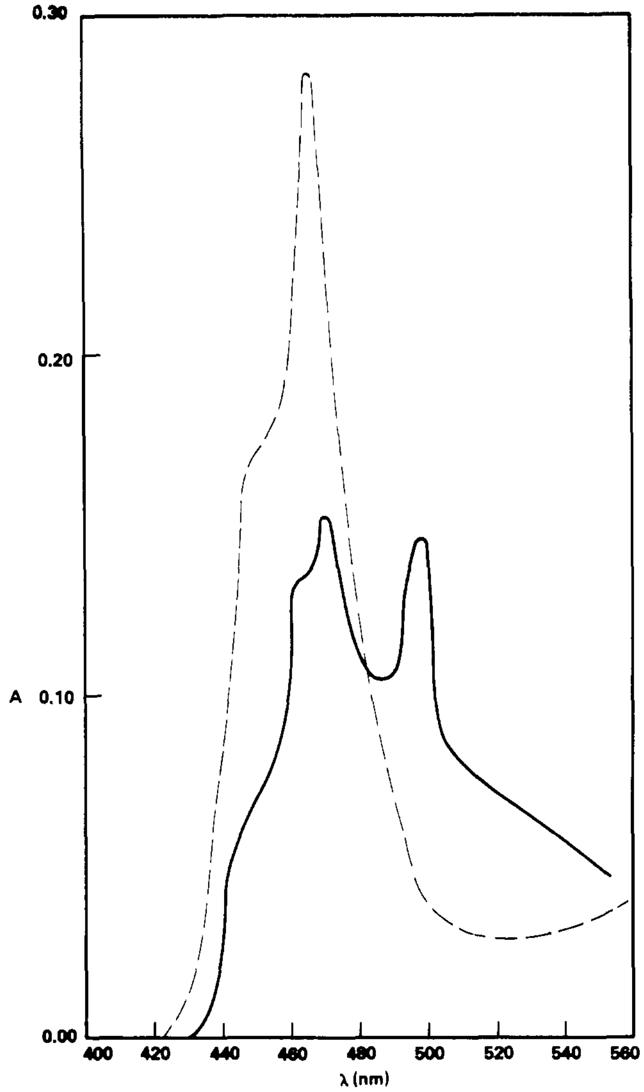


Figure 4. Absorption spectrum from 3.0×10^{-4} M DCA + 0.05 M TS + 1.0×10^{-3} M TPE, 1 μs after laser pulse, in air-saturated CH_3CN (—). - - - is the same as in Figure 3 under air, no TPE.

for the suggestion that radical ions are intermediate in the cyanoaromatic-sensitized photooxidation. It also suggests that oxygen reacts very rapidly with the sensitizer radical anion, most likely forming $O_2^{-}\cdot$. The small change in the lifetime of the radical cation in going from N_2- to air-saturated solution implies that direct reaction of oxygen with the radical cation (Barton mechanism)[21,22] is comparatively slow under air. However, it may be somewhat more important under O_2, where there is a considerable decrease in the lifetime of the radical cation. Thus, although other mechanisms for the formation of oxidation products are not ruled out, the mechanism suggested[4] is consistent with the observed facts.

References and Notes

(1) Paper 2 is ref 4b. Supported by NSF Grant CHE 77-21560.
(2) (a) R. A. Neunteufel and D. R. Arnold. *J. Am. Chem. Soc.*, **95,** 4080 (1973); (b) D. R. Arnold and Y. Shigemitsu, *J. Chem. Soc., Chem. Commun.*, 407 (1975); (c) A. J. Maroulis and D. R. Arnold, *J. Am. Chem. Soc.*, **98,** 5931 (1976); (d) A. Maroulis, Y. Shigemitsu, and D. R. Arnold, *ibid.*, **100,** 535 (1978); (e) R. Humphreys and D. R. Arnold, *ibid.*, **101,** 2743 (1979).
(3) K. A. Brown-Wensley, S. Mattes, and S. Farid, *J. Am. Chem. Soc.*, **100,** 4162 (1978).
(4) (a) J. E. Eriksen, C. S. Foote, and T. L. Parker, *J. Am. Chem. Soc.*, **99,** 6455 (1977); (b) J. Eriksen and C. S. Foote, *J. Phys. Chem.*, **82,** 2659 (1978).
(5) In the case of *trans*-stilbene the products are benzaldehyde (53%), stilbene epoxide (20%), benzil (24%), and 4% *cis*-stilbene.[4,6] The benzaldehyde is believed to be formed from cleavage of the corresponding dioxetane, which is not stable under the reaction conditions.[7]
(6) J. Eriksen and C. S. Foote, manuscript in preparation.
(7) P. M. Allen and C. S. Foote, unpublished work.
(8) The sensitizer is excited by a Quanta-Ray DCR-1 Nd-YAG laser and amplifier at 355 nm, 100 mJ/pulse, 10-Hz rate, 10-ns pulse duration. A xenon flash lamp (manufactured in house) is used as the probe. The flash is focused on a 1 × 1 × 5 cm quartz cuvette and then passed to a Jobin-Yvon 4-137 UV monochromator (1-mm slit, 4–8-nm band pass) fitted with a modified[23] 1P28 photomultiplier tube. The phototube anode current remains linear up to 15 mA for 1.5 ms. In most cases, a 50-Ω load resistor is used at the photomultiplier, giving ≤10-ns time response. The voltage across the load resistor is displayed on a Tektronix 7904 oscilloscope with a 7B92 time base, a 7A24 vertical amplifier, and a PG 201 FET probe. For absorption spectra, the oscilloscope traces are recorded on a Tektronix C-51 oscilloscope camera and analyzed by hand, point by point. For kinetic analysis, the output of the photomultiplier is fed into a Biomation 805 wave-form digitizer, the output from which is analyzed by a PDP 11/45 computer using programs written by W. Hopewell and Dr. L. Levine, UCLA. In experiments using a longer time base, the flash lamp is replaced with an Eimac 150-W xenon lamp and a Uniblitz 225 shutter. Some confirming experiments were performed at the Center for Fast Kinetics Research in Austin, Texas. Dr. M. A. J. Rodgers and J. Becker provided valuable assistance. The system has been described.[24] All of the work reported here was performed at UCLA.
(9) W. Hamill, "Radical Ions," E. T. Kaiser and L. Kevan, Eds., New York Intersciences, New York, 1968, p 405.
(10) T. Shida and W. Hamill, *J. Chem. Phys.*, **44,** 2375 (1966).
(11) M. A. J. Rodgers, *Faraday Soc. Trans.*, **67,** 1029 (1971).
(12) $DCA^{-}\cdot$ and $CA^{-}\cdot$ were generated by adding Na to DCA and CA, respectively, using THF distilled from Na and benzophenone in a modification of the procedure given in D. Paul, D. Upkin, and S. I. Weisman, *J. Am. Chem. Soc.*, **78,** 116 (1956). Absorption spectra were taken of these solutions.
(13) ESR spectra were measured on a Varian E-12 spectrometer. The excitation source was a Eimac 150-W xenon lamp focused on the spectrometer cavity after passing through a 400–450-nm band-pass filter consisting of 28 g of $CuSO_4 \cdot 5H_2O$, 30 g of $NaNO_2$, and 50 mL of concentrated NH_4OH in 1 L of H_2O.[25] The spectra were recorded at ambient temperature in N_2-saturated dry MeCN.
(14) J. W. Happ and E. G. Janzen, *J. Org. Chem.*, **35,** 96 (1970).
(15) A. P. Schaap, K. A. Zaklika, B. Kaskar, and L. W.-M. Fung, *J. Am. Chem. Soc.*, preceding paper in this issue. We thank Professor Schaap for a prepublication copy of his manuscript.
(16) Potentials were measured vs. SCE in acetonitrile by cyclic voltammetry by Dr. J. Eriksen and Dr. Pauline M. Allen.
(17) A. Zweig, W. G. Hodgson, and W. H. Jura, *J. Am. Chem. Soc.*, **86,** 4124 (1964).
(18) D. Rehm and A. Weller, *Isr. J. Chem.*, **88,** 1686 (1966).
(19) W. R. Ware, J. D. Holms, and D. R. Arnold, *J. Am. Chem. Soc.*, **96,** 7861 (1974).
(20) The spectrum from *trans*-stilbene does not show an absorption band corresponding to $CS^{+}\cdot$ (spectra taken from 1–10 μs after the laser flash) even though *cis*-stilbene is observed as a product in the DCA photosensitized oxidation of *trans*-stilbene.[6] Evidently during the time of the laser flash experiment there is not sufficient time to accumulate a detectable amount of *cis*-stilbene.
(21) D. H. R. Barton, G. LeClerc, P. D. Magnus, and I. D. Menzies, *J. Chem. Soc., Perkin Trans. 1*, 2055 (1975).
(22) R. Tang, H. J. Yue, J. F. Wolf, and F. Mares, *J. Am. Chem. Soc.*, **100,** 5248 (1979).
(23) J. Hunt and J. K. Thomas, *Radiat. Res.*, **32,** 149 (1967).
(24) B. A. Lindig and M. A. J. Rodgers, *J. Phys. Chem.*, **83,** 1685 (1979).
(25) J. L. Calvert and J. N. Pitts Jr., "Photochemistry", Wiley, New York, 1966, p 737.

Lonnie T. Spada, Christopher S. Foote*
Department of Chemistry, University of California
Los Angeles, California 90024

Received September 4, 1979

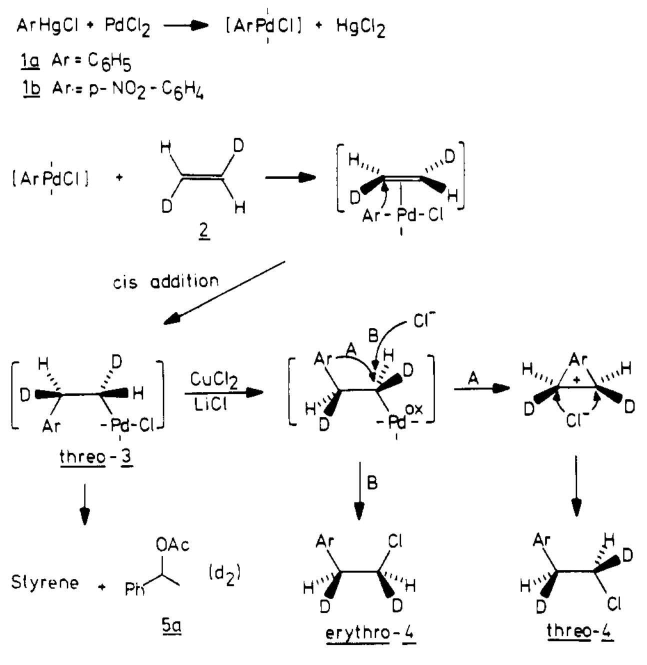
Phenyl Participation in the Cleavage of β-Phenethyl–Palladium Bonds by Cupric Chloride

Sir:

Although oxidative cleavage of transition metal–carbon bonds has been studied extensively,[1-8] the detailed mechanism of such reactions is still unclear. Stereochemical studies on oxidative cleavage processes have shown both inversion[3-6] and retention[6,7] of configuration at carbon as well as lack of stereospecificity.[1,8]

One oxidative cleavage reaction that has been a matter of much speculation is the cupric halide cleavage of palladium–carbon bonds, in which palladium is replaced by halide.[5,8,9] This cleavage reaction has been proposed to proceed either by reductive elimination,[10] a radical mechanism,[1,8] or an ionic mechanism involving nucleophilic displacement at carbon.[5,9e] Budnik and Kochi observed loss of stereochemistry in the cu-

Scheme I



pric bromide cleavage of nortricyclyl-palladium bonds.[8] We have recently found that such copper(II)-induced cleavage of β-oxoalkyl-palladium bonds occurs with predominant inversion at carbon.[5]

To obtain further information on the cupric chloride cleavage, we studied the cleavage of 2-phenethyl-palladium bonds. Phenyl participation has recently been observed in the oxidative cleavage (halogenation) of 2-phenethyl-iron bonds.[11] To the best of our knowledge this is the only reported case on phenyl participation in the cleavage of metal-carbon bonds. Analogous participation in the cupric chloride cleavage would provide information on carbonium ion character at carbon. In this communication we report that phenyl participation takes place in the cupric chloride cleavage of 2-phenethyl-palladium bonds, indicating that carbonium-ion character is important in the cleavage process.

Stereochemical studies on the cleavage of 2-arylethyl-palladium bonds were done as shown in Scheme I. The arylpalladium chloride, generated in situ from arylmercuric chloride **1**, was reacted with (*E*)-1,2-dideuterioethene (**2**)[12] in the presence of cupric chloride, following the description by Heck.[9c] In this way **1a** and **2** gave *threo*-1,2-dideuterio-2-phenethyl chloride (*threo*-**4a**), deuterated styrenes, and 1-phenethyl acetate-d_2 (**5a**). The configurational assignment of *threo*-**4a** was done by NMR.[11b] Using *p*-nitrophenylpalladium chloride, derived from **1b**,[13] as the arylating agent gave a mixture of *erythro*- and *threo*-**4b** with *erythro*-**4b** as the major diastereoisomer, together with *p*-nitrostyrene. Results from arylations of deuterated ethene are given in Table I.

A probable mechanism that accounts for these results is shown in Scheme I. The arylpalladium chloride reacts with the olefin **2** to produce an intermediate organopalladium adduct **3**. Cis addition of arylpalladium to olefins is well documented[14] and would in our case give *threo*-**3**. Oxidative cleavage of the palladium-carbon bond in **3** by cupric chloride would produce the halide **4**, and β-elimination of hydrogen would give the styrenes. Formation of *threo*-**4a** indicates that the oxidative cleavage has occurred with retention in this case, which at first appears to support a mechanism involving a 1:2 shift of chlorine from palladium to carbon (reductive elimination) proposed by Heck.[10] However, this would conflict with our previous results, which showed[5] that the $CuCl_2$-LiCl cleavage of the palladium-carbon bond in oxypalladation adducts takes place with predominant inversion of configuration at carbon.

An explanation that accounts for the observed retention at carbon in the phenyl case, consistent with our previous results,[5] is that the phenyl group participates (path A), resulting in the formation of a symmetrical phenonium ion. Chloride attack on either methylene group of the phenonium ion would then give *threo*-**4a**. The formation of *erythro*-**4b** as the major isomer from the *p*-nitro-substituted compound is consistent with the expected weaker participation of the *p*-nitrophenyl group. In this case the competing nucleophilic displacement of the metal by chloride becomes the main path (path B).

To obtain more convincing evidence that phenyl participation is responsible for the stereochemical results found here, we studied the reaction of $PhCH_2CD_2HgCl$ (**6**)[15] in the presence of palladium(II) and copper(II) (eq 1). In this reac-

$$\underset{\textbf{6}}{PhCH_2CD_2HgCl} \xrightarrow{PdCl_4^{2-}} \underset{\textbf{7}}{\left[PhCH_2CD_2PdCl\right]}$$

$$\xrightarrow[LiCl]{CuCl_2} \underset{\substack{\textbf{8}\\1}}{PhCH_2CD_2Cl} \; + \underset{\substack{\textbf{9}\\1}}{PhCD_2CH_2Cl} \quad : \qquad (1)$$

tion an intermediate phenethylpalladium complex **7** is expected by a metal exchange, which could react with the cupric chloride present. Using similar reaction conditions to those above (45 °C, 16 h, acetic acid-water (90:10),$[PdCl_2] = 0.04$ M, $[CuCl_2] = 2$ M, $[LiCl] = 5$ M), **6** gave a mixture of **8** and **9** in ratio of 1:1 (yield, 25%). A control experiment showed that **8** is stable under the reaction conditions and does not rearrange to **9**. Furthermore reaction of **6** with $CuCl_2$-LiCl, in the absence of palladium chloride, gave only traces of 2-phenethyl chloride (<1%) under the same reaction conditions. Thus the formation of **8** and **9** in approximately equal amounts is good evidence for a symmetrical phenonium-ion intermediate in the cupric chloride cleavage of **7**.

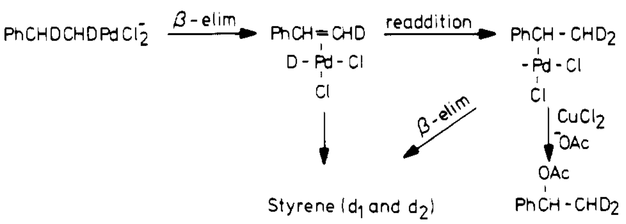
Analysis of **5a** from the reaction of **1a** and deuterated ethene

Table I. Palladium-Catalyzed Arylation of (*E*)-1,2-Dideuterioethene (**2**) in the Presence of $CuCl_2$-LiCl[a]

organopalladium intermediate	$[CuCl_2]$, M	[LiCl], M	time, h	product yield, %[b]		
				4	styrenes	**5**
$C_6H_5CHDCHDPdCl$	0.5	0.25	27	20 (threo)[c]	25	25
$C_6H_5CHDCHDPdCl$	2	1	19	50 (threo)[c]	15	15
$C_6H_5CHDCHDPdCl$	2	5	4	80 (threo)[c]	traces	traces
p-$NO_2C_6H_4CHDCHDPdCl$	2	1	18	20[d,e]	30[e]	
p-$NO_2C_6H_4CHDCHDPdCl$	2	5	18	30[d,e]	traces	

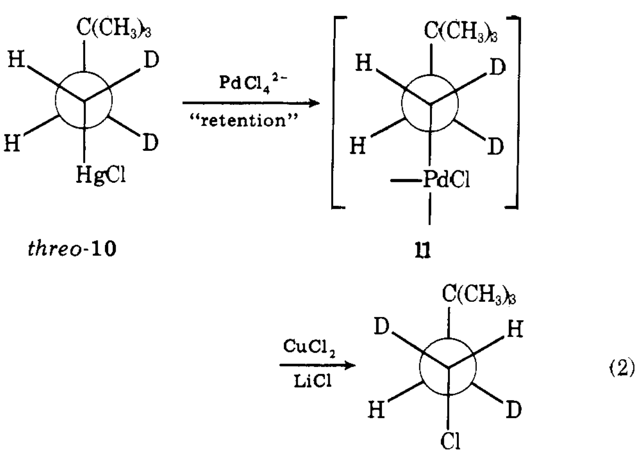
[a] The reactions were performed at 20 °C in acetic acid-water (90:10) containing 0.01 M palladium chloride. The initial gauche pressure of **2** was 3-4 kg/cm^2. [b] Determined by gas chromatography unless otherwise noted. [c] Only the threo isomer (>95%) was observed. [d] The configurational assignment could not be obtained directly from the NMR spectrum of **4b** because J_{HH}(threo)-J_{HH}(erythro) = <0.3 Hz. However, conversion ($SnCl_2$/HCl) of **4b** into *p*-$NH_2C_6H_4CHDCHDCl$ and NMR analysis of the converted product indicated that *erythro*-**4b** was the major diastereoisomer. [e] Isolated yield.

Scheme II



2 indicates that this compound is formed by a β-elimination–readdition sequence similar to that proposed[5b,16] in the Wacker process, followed by cleavage of the palladium–carbon bond by acetate.[9a,17] The expected acetates **5a** from such a sequence are PhCH(OAc)CHD$_2$ and PhCD(OAc)CH$_2$D. The sequence for the formation of the former acetate is given in Scheme II. NMR analysis of the isolated acetate mixture **5a** indicated the presence of a benzyl proton from only one compound, and, more importantly, this proton appears as a doublet.[18] Evidently, the deuterium content is retained in the molecule, which eliminates a path involving acetic acid addition to free styrene.

For comparison we have also studied the stereochemistry of the cupric chloride cleavage of a palladium–carbon bond in one case where participation of any kind is excluded (eq 2).



erythro-**12** (>85% erythro)

The mercury compound *threo*-**10**[19] was used to generate an intermediate palladium compound **11.** Reaction of *threo*-**10**, using the same conditions as those employed above for reaction of **6**, gave the chloride *erythro*-**12.**[20] Since alkyl transfer from mercury to palladium is known[21] to take place with retention, the results show that in this case the cleavage of the palladium–carbon bond has occurred with inversion.

Acknowledgment. We are grateful to the Swedish Natural Science Research Council and "Stiftelsen Bengt Lundqvists minne" for financial support.

References and Notes

(1) J. K. Kochi "Organometallic Mechanisms and Catalysis", Academic Press, New York, 1978.

(2) (a) P. M. Henry, *Adv. Organomet. Chem.*, **13,** 363 (1975); (b) M. D. Johnson, *Acc. Chem. Res.*, **11,** 57 (1978).

(3) (a) S. N. Anderson, D. H. Ballard, J. Z. Chrazastowski, D. Dodd, and M. D. Johnson, *J. Chem. Soc., Chem. Commun.*, 685 (1972); (b) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96,** 2814 (1974).

(4) (a) J. E. Bäckvall, *Tetrahedron Lett.*, 163 (1978); (b) J. E. Bäckvall, *J. Chem. Soc., Chem. Commun.*, 413 (1977); (c) R. H. Magnuson, J. Halpern, I. Ya. Levitin, and M. E. Volpin, *ibid.*, 44 (1978).

(5) (a) J. E. Bäckvall, *Tetrahedron Lett.*, 467 (1977); (b) J. E. Bäckvall, B. Akermark, and S. O. Ljunggren, *J. Am. Chem. Soc.*, **101,** 2411 (1979).

(6) (a) P. K. Wong and J. K. Stille, *J. Organomet. Chem.*, **70,** 121 (1974); (b) D. Dong, B. K. Hunter, and M. C. Baird, *J. Chem. Soc., Chem. Commun.*, 11 (1978).

(7) (a) I. J. Harvie and F. J. McQuillin, *J. Chem. Soc., Chem. Commun.*, 241 (1977); (b) J. A. Labinger, D. W. Hart, W. E. Seibert, and J. Schwartz, *J. Am. Chem. Soc.*, **97,** 3851 (1975); (c) R. W. Johnson and R. G. Pearson, *Chem. Commun.*, 986 (1970).

(8) R. A. Budnik and J. K. Kochi, *J. Organomet. Chem.*, **116,** C3 (1976).

(9) (a) P. M. Henry, *J. Org. Chem.*, **39,** 3871 (1974); (b) H. Stangl and R. Jira, *Tetrahedron Lett.*, 3589 (1970); (c) R. F. Heck, *J. Am. Chem. Soc.*, **90,** 5538 (1968); (d) A. Heumann and B. Waegell, *Nouv. J. Chim.*, **1,** 277 (1977); (e) D. Clark, P. Hayden, and R. D. Smith, *Discuss. Faraday Soc.*, **46,** 98 (1968).

(10) R. F. Heck, "Organotransition Metal Chemistry", Academic Press, New York, 1974, p 110.

(11) (a) T. C. Flood and F. J. Disanti, *J. Chem. Soc., Chem. Commun.*, 18 (1975); (b) D. A. Slack and M. C. Baird, *J. Am. Chem. Soc.*, **98,** 5539 (1976).

(12) Prepared according to P. P. Nicholas and R. T. Carrol, *J. Org. Chem.*, **33,** 2345 (1968).

(13) Prepared according to A. N. Nesmejanow, N. T. Gluschnew, P. T. Epifansky, and A. I. Flegontow, *Chem. Ber.*, **67,** 130 (1934).

(14) (a) P. M. Henry, *Acc. Chem. Res.*, **6,** 16 (1973); (b) P. M. Henry and G. A. Ward, *J. Am. Chem. Soc.*, **94,** 673 (1972); (c) R. F. Heck, *Acc. Chem. Res.*, **12,** 146 (1979); (d) S. I. Murahashi, M. Yamamura, and N. Mita, *J. Org. Chem.*, **42,** 2870 (1977).

(15) Prepared from the Grignard reagent of **8** and mercuric chloride. The deuterated chloride **8** was prepared by reaction of 1,1-dideuterio-2-phenethyl alcohol with thionyl chloride. The alcohol was prepared by a known procedure: W. H. Saunders, S. Asperger, and D. H. Edison, *J. Am. Chem. Soc.*, **80,** 2421 (1958).

(16) R. Jira, J. Sedlmeier, and J. Smidt, *Justus Liebigs Ann. Chem.*, **693,** 99 (1966).

(17) (a) P. M. Henry, *J. Am. Chem. Soc.*, **94,** 7305 (1972); (b) J. E. Bäckvall, *Tetrahedron Lett.*, 2225 (1975).

(18) NMR analysis indicated a ratio of PhCH(OAc)CHD$_2$ to PhCD(OAc)CH$_2$D of 1:1.9, which reflects the isotope effect in the β-elimination.

(19) (a) M. Gielen and R. Fosty, *Bull. Soc. Chim. Belg.*, **83,** 333 (1974); (b) R. C. Larock and H. C. Brown, *J. Am. Chem. Soc.*, **92,** 2467 (1970).

(20) Configurational assignment of **12** was based on its NMR spectrum: G. M. Whitesides, J. P. Sevenair, and R. W. Goets, *J. Am. Chem. Soc.*, **89,** 1135 (1967).

(21) (a) J. E. Bäckvall and B. Åkermark, *J. Chem. Soc., Chem. Commun.*, 82 (1975); (b) J. K. Stille and P. K. Wong, *J. Org. Chem.*, **40,** 335 (1975).

Jan-E. Bäckvall,* Ruth E. Nordberg
Department of Organic Chemistry
Royal Institute of Technology, S-100 44 Stockholm, Sweden

Received July 26, 1979

Proton Nuclear Magnetic Resonance Characterization of the Electronic Structure of Horseradish Peroxidase Compound I

Sir:

The detailed electronic structures of the reactive forms[1] of horseradish peroxidase compound I (HRP-I) and compound II (HRP-II) have remained unresolved despite extensive research in the past few years, largely because of the apparently contradictory evidence from a number of spectroscopic or physical measurements.[2-8] Susceptibility data,[2] as well as Mössbauer[3-5] and EPR[5] studies, support the low-spin (ls) iron(IV) configuration for both the green HRP-I and red HRP-II, which are 2 and 1 oxidizing equiv[1] above the resting enzyme, HRP. The inferred free-radical nature of the second oxidizing equivalent[1] in HRP-I has been attributed to the presence of a porphyrin cation radical based on their optical spectra.[6] The observation of an anomalous ESR signal[5,7] is not inconsistent with this proposal, although a spin-coupled amino acid centered radical, similar to that reported for the cytochrome *c* peroxidase ES complex,[9] has also been suggested.[7]

The recently reported[8] ^{1}H NMR spectrum of HRP-I, however, has been interpreted as providing strong evidence against a porphyrin cation radical and for a high-spin (hs) iron(IV).[10] We present here new ^{1}H NMR data on deuterohemin-reconstituted[11] horseradish peroxidase compound I (deutero-HRP-I) which provide an alternative interpretation that is consistent with a ls iron(IV) cation radical formulation for compound I.

Deuterohemin was reconstituted into apo-HRP and purified

0002-7863/80/1502-0395$01.00/0