Table I. Spectra of Heme Compounds I–IV and Deuteromyoglobin Derivatives

	Reduced			CO			O_2		Met (pH 7)		
	Soret	β	α	Soret	β	α	Soret	α	Soret	β	α
Deuteromyoglobin[a]	421	544		409	528	554	532	565	393	496	620
Compounds I–IV[b] (CH_2Cl_2) (25°)		545		412	528	555					
Compounds I–IV[b] (CH_2Cl_2) (−45°)		517	545	412	527	556	530	562	388	500	628
Compounds I–IV (solid)[c]		522	548	412	528	555	530	564	389	500	628

[a] A. Rossi-Fanelli and E. Antonini, *Arch. Biochem. Biophys.*, **72**, 243 (1957). [b] This work. [c] Reference 1.

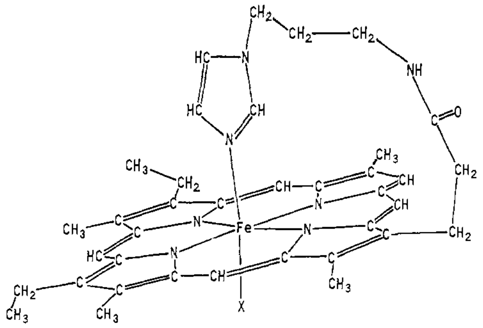

Figure 1. Structure of pyrroheme-*N*-[3-(1-imidazolyl)propyl]-amide and its derivatives: I, X = no substituent or H_2O, Fe^{II}; II, X = Cl, Fe^{III}; III, X = O_2, Fe^{II}; IV, X = CO, Fe^{II}.

−45° in a liquid propane bath precipitated the water and caused the broad peak at 545 nm to split into two sharp peaks at 517 and 545 nm (Figure 2A). When oxygen was admitted to this solution at −45°, an immediate color change occurred and spectrum 2B was obtained. Replacing the oxygen atmosphere over the solution with carbon monoxide resulted in spectrum 2C, and a brief photolysis with a General Electric photoflood under vacuum produced spectrum 2D, identical with 2A.[4] When the carbon monoxide complex having spectrum 2C was warmed to room temperature, no change occurred. Addition of excess pyridine to the oxygen complex at −45° resulted in a typical pyridine–hemochrome spectrum.

Warming the oxygen complex III to room temperature resulted in the oxidation of the heme to give II.

The maxima for the α and β peaks in Figure 2 are listed in Table I along with those of deuteromyoglobin.[4]

These experiments clearly show, contrary to a number of previous conclusions, that this simple heme compound reversibly binds oxygen in solution and that the iron is not oxidized. We attribute the successful oxygen complexation to two factors. First, the neighboring group effect of the covalently attached imidazole increases oxygen binding. Secondly, the reaction

$$\text{heme-}O_2\text{ (III)} + \text{heme (I)} \longrightarrow 2\text{hemin (II)} \qquad (1)$$

apparently has an activation energy which causes this reaction to be very slow at low temperature. This activation energy, combined with the reduction of the concentration of free heme in solution, causes a severe reduction in the rate of heme oxidation.

The striking similarity of the spectra of compounds I, III, and IV to the deoxy, oxy, and carboxy forms of deuteromyoglobin seen in Table I strongly support the proposed one-to-one stoichiometry of complex III and

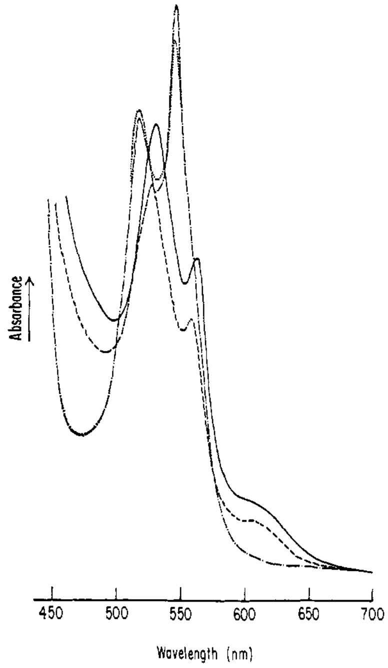

Figure 2. Visible spectra of a methylene chloride solution of pyrroheme-*N*-[3-(1-imidazolyl)propyl]amide (II) and its derivatives at −45° as described in the text and in Figure 1: (A) —·—·—, I, from dithionite reduction; (B) —, III, obtained by adding oxygen to I; (C) - - -, IV, from replacing O_2 gas with CO gas; (D) . . . ., I, obtained from photolysis of IV.

the theory[1] that simple biological reactions such as oxygen binding do not require the protein.

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(4) In a separate experiment, the oxygen complex was filtered at −45° to remove the ice and excess dithionite before the remaining experiments were done. The results were the same as those with the unfiltered sample.

Mechanism of 1,5-Hydrogen Migration in Diene Iron Carbonyl Complexes

Sir:

We wish to report a mechanistic investigation of a novel rearrangement of diene iron tricarbonyl complexes. When any of a variety of substituted cyclohexadiene–iron tricarbonyl complexes are heated in refluxing xylene for several hours, isomerization resulting from 1,5-hydrogen migration is observed. For example, the phenyl substituted compound **1**[1] is

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(1) This compound[2] was prepared as a mixture with **2**[2] by photolysis of phenylcyclohexadiene[3] with $Fe(CO)_5$. The isomers were separable by column chromatography on alumina.

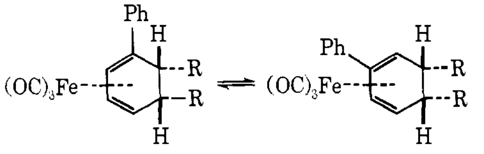
(2) This compound had acceptable elemental analysis.

(3) C. F. Woods, N. C. Bolgiano, and D. E. Duggan, *J. Amer. Chem. Soc.*, 77, 1802 (1955).

Table I. Appearance of Isomerized and Scrambled Products from 1-d_2 and 2-d_2

Time, hr	1-d_2[a]		1-s[b]		2-d_2[a]		2-s[b]	
	Obsd[c]	Calcd[c,d]	Obsd[c]	Calcd[c,d]	Obsd[c]	Calcd[c,d]	Obsd[c]	Calcd[c,d]
0	100		0		0		0	
3	52 ± 7	(52)	9 ± 5	3	15 ± 8	15	25 ± 10	30
24	32 ± 5	(32)	13 ± 7	8	20 ± 10	11	44 ± 10	40
0	0		0		100		0	
8	13 ± 5	10	2 ± 2	5	74	(74)	10 ± 5	11
24	11 ± 5	11	12 ± 5	8	60	(60)	20 ± 10	21

[a] 1-d_2 and 2-d_2 refer to stereospecifically labeled **1** and **2**. [b] 1-s and 2-s refer to **1** and **2** with deuterium scrambled. [c] Entries in per cent. [d] These values are calculated using the kinetic scheme and rate constants shown in the text.



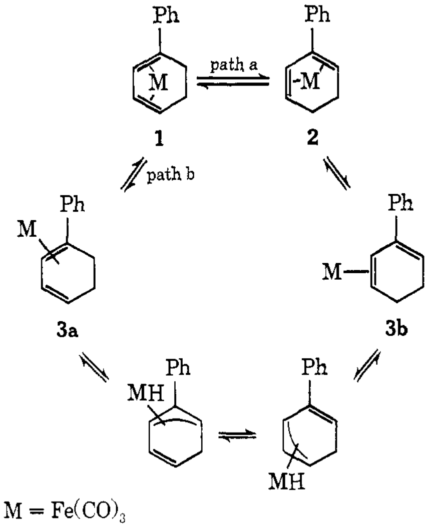
1, R = H
1-d_2, R = D

2, R = H
2-d_2, R = D

isomerized to an equilibrium mixture of **1** and **2** (K_{eq} = **2**/**1** = 3.35 ± 0.1) with a half-life of about 4 hr at 145° (xylene solvent, sealed tube).

We have considered two possibilities for the mechanism of this reaction: (a) a concerted 1,5 sigmatropic shift of hydrogen or (b) a pathway involving intermediate formation of a metal hydride (Scheme I).

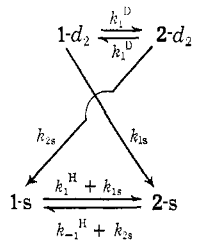
Scheme I



Our approach to distinguishing these paths was based on the expectation that the concerted sigmatropic shift (path a) should display a considerable isotope effect and might not be restricted to hydrogens cis to the metal. The metal hydride pathway (path b) would, on the other hand, necessarily involve cis hydrogens and would not show a large isotope effect if rate-determining formation of a coordinatively unsaturated intermediate is involved prior to hydrogen abstraction.

The labeled compounds necessary for the experiments suggested by these expectations were readily available by the method of Whitesides and Arhart.[4] Thus, a mixture of **1**-d_2 and **2**-d_2, stereospecifically labeled with deuterium cis to the metal in the methylene groups, was prepared by exchange with trifluoroacetic-*O*-d_1 acid. These compounds were separated and subjected to the isomerization conditions. The resulting mixtures were analyzed as a function of time by a combination of high-pressure liquid chromatography and nmr. In fact, scrambling of the deuterium was observed to be quite rapid (see Table I). In addition, a mixture of **1**-d_2 and **1** (d_0/d_2 = 1.09 ± 0.03 by mass spectrometry) was isomerized under the reaction conditions to the extent of 8 ± 2%. Species **2** was isolated and the ratio d_0/d_2 was found to be 1.37 ± 0.05, indicating a small but measurable isotope effect on the disappearance of **1** (*vide infra*). These data were analyzed in terms of the scheme shown below (Scheme II). Numerical integration[5] of the differential equations corresponding to this scheme gave the best fit (Table I) to the experimental data with the parameters shown; the estimated error in these values is approximately 50%. In particular, the experimental points could not be duplicated with an isotope effect greater than about 2.5. This isotope effect is smaller than would be expected for a concerted 1,5 shift.[6] We suggest, therefore, that the cis hydrogen shift, at least, occurs principally by path b.[7]

Scheme II



$k_1^D = 4$
$k_{-1}^D = 2$
$k_{1s} = 8$
$k_{2s} = 1$

$$1 = \frac{k_1^H}{k_1^D} \cong \frac{k_{-1}^H}{k_{-1}^D} = 2$$

Direct evidence for a coordinatively unsaturated intermediate such as **3** was obained by a trapping experiment. The 1-phenyl isomer **1** was heated in the presence of a tenfold excess of triphenylphosphine. Conditions which gave 35% **2** from **1** in the absence of phosphine gave only 5% total isomerized product in the presence of phosphine. In addition, a 71% yield of bis(triphenylphosphine)iron tricarbonyl was formed. These results are consistent with the trapping of intermediate **3** by phosphine at a rate slightly faster than, but competitive with, hydrogen abstraction. The data are not consistent with the reaction of **1**

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(4) T. H. Whitesides and R. W. Arhart, *J. Amer. Chem. Soc.*, **93**, 5296 (1971).

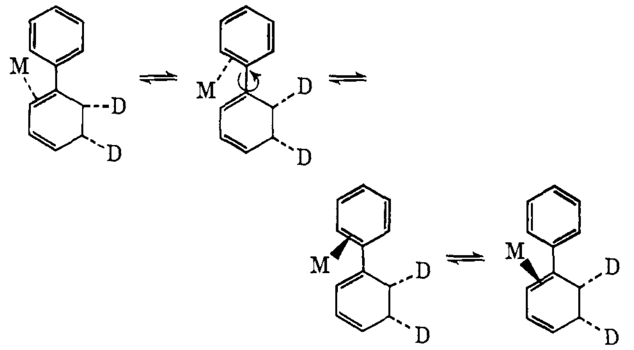
(5) These calculations were carried out using a program written for a Wange Model 720C programmable calculator equipped with a *XY* plotter. We thank Professor Howard Whitlock of this department for the use of this machine.

(6) W. R. Roth and J. Konig, *Justus Liebigs Ann. Chem.*, **699**, 24 (1966); H. Kloosterziel and A. P. ter Borg, *Recl. Trav. Chim. Pays-Bas*, **84**, 1305 (1965), have found values of k_H/k_D of 5–7 for concerted 1,5 shifts.

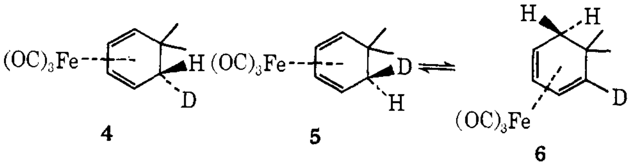
(7) The occurrence of an appreciable (small) isotope effect in this case can be rationalized by the reversibility of the formation of the coordinatively unsaturated intermediate.

with phosphine by an unrelated path; in this case, the amount of isomerized product formed must be greater than 10%.[8]

Remaining is the question of deuterium scrambling in these complexes. We feel that this result does not require a pathway involving exo migration of hydrogen. Instead, the phenyl ring provides a way in which the iron atom can migrate from one side of the cyclohexadiene ring to the other. Victor, Ben-Shoshan, and Sarel[9,10] have shown that aromatic rings can coordinate $Fe(CO)_3$ to give diene complexes; our results indicate that an aromatic ring may coordinate the unsaturated $Fe(CO)_3$ fragment as well. In fact, the relative rate constants shown in Scheme II demonstrate that migration of the iron atom onto the aromatic ring is quite competitive with hydrogen abstraction.



That the presence of the aryl group is necessary for scrambling is consistent with the observation that no observable incorporation of deuterium into the vinyl region takes place in compound **4**,[11] while **5**[11] equilibrates readily with **6** at 145°. The rate of isomerization is at least 125 times faster than that of the rate of scrambling in these species.



4 **5** **6**

Whitlock and coworkers[12] have postulated intermediates analogous to **3** to account for hexatriene–iron tricarbonyl complex isomerization, which takes place under conditions similar to our hydrogen migration. The postulated metal hydride is the same kind of intermediate demonstrated[13] to account for double bond isomerization catalyzed by iron carbonyls again under similar conditions of thermal activation. An authenticated example of a concerted sigmatropic shift in the coordination sphere of a transition metal thus remains to be discovered.

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[8] If the $(Ph_3P)_2Fe(CO)_3$ is formed by an unrelated pathway (*i.e.*, ligand exchange), then the remainder of the complex should have undergone 35% isomerization. Thus, the amount of 2-phenyl isomer formed must be substantially greater than (0.35)(29) = 10%.

[9] R. Victor, R. Ben-Shoshan, and S. Sarel, *J. Org. Chem.*, 37, 1930 (1972).

[10] R. Victor, R. Ben-Shoshan, and S. Sarel, *Tetrahedron Lett.*, 4257 (1970).

[11] Compound **5** was prepared by sodium cyanoborodeuteride reduction of 6,6-dimethylcyclohexadienyliron tricarbonyl tetrafluoroborate, while **4** was prepared by corresponding reduction with sodium cyanoborohydride, followed by exchange with CF_3CO_2D.

[12] H. W. Whitlock and R. L. Markezich, *J. Amer. Chem. Soc.*, **93**, 5290, 5291 (1971); H. W. Whitlock, C. Reich, and W. P. Woessner, *ibid.*, **93**, 2483 (1971); H. W. Whitlock and Y. N. Chuah, *ibid.*, **87**, 3605 (1965).

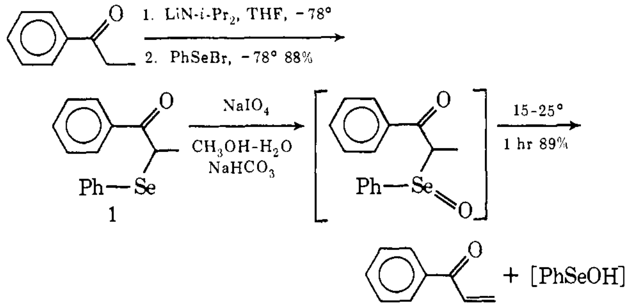
[13] C. P. Casey and C. R. Cyr, *ibid.*, **95**, 2248 (1973). We thank Professor Casey for a preprint of his manuscript.

Organoselenium Chemistry. α-Phenylseleno Carbonyl Compounds as Precursors for α,β-Unsaturated Ketones and Esters

Sir:

We report here a method for the conversion of ketones and esters to their α,β-unsaturated derivatives. The method is based on our observation that lithium enolates react rapidly and cleanly with benzeneselenenyl halides to give α-phenylseleno carbonyl compounds and on the report by Jones, Mundy, and Whitehouse[1] that aliphatic selenoxides readily undergo β-elimination to form olefins. Sharpless and Lauer[2] have recently applied this facile elimination in the synthesis of allyl alcohols from epoxides.

The method is illustrated for the conversion of propiophenone to acrylophenone,[3,3a] an olefin unusually sensitive to polymerization and nucleophilic attack. The selenide **1** can be isolated by crystallization in 88% yield (mp 36.5–37°, ir ν_{CCl_4} 1675 cm^{-1}; nmr δ_{CCl_4} 1.60 (d, J = 7.0 Hz, 3 H), 4.59 (q, J = 7.0 Hz, 1 H), 7.1–7.6 (m, 8 H), 7.88 (dd, J = 2, 8 Hz, 2 H)). Oxidation of **1** with sodium metaperiodate results in conversion to acrylophenone (89% yield).



The reaction of lithium enolates with benzeneselenenyl bromide or chloride[4] to give α-phenylseleno carbonyl compounds can be performed in high yield in a variety of esters and ketones. In all cases described here, this reaction was instantaneous at −78° and is

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[1] D. N. Jones, D. Mundy, and R. D. Whitehouse, *Chem. Commun.*, 86 (1970).

[2] K. B. Sharpless and R. F. Lauer, *J. Amer. Chem. Soc.*, **95**, 2697 (1973).

[3] A related method involving β-elimination of α-methyl sulfinyl esters has been developed by B. M. Trost and T. Salzmann (private communication).

(3a) NOTE ADDED IN PROOF. Professor K. B. Sharpless has informed us of his independent work on the synthesis of α,β-unsaturated carbonyl compounds using organoselenium reagents.

[4] (a) Benzeneselenenyl bromide can be prepared by the addition of bromine to diphenyl diselenide in tetrahydrofuran or other nonhydroxylic solvents. This solution can be used directly. Benzeneselenenyl chloride works equally well but is not as conveniently prepared. (b) Enol acetates and enol silanes react with selenenyl derivatives to give α-arylseleno carbonyl compounds, and this provides an alternative synthesis. See also G. Hölzle and W. Jenny, *Helv. Chim. Acta*, **41**, 593 (1958).