Phenylphosphonate **1** was synthesized in five steps from triethyl phosphite and methyl 5-bromopentanoate.[18] Phosphonate **1** was coupled to the carrier proteins bovine serum albumin (BSA) and keyhole limpet hemocyanin (KLH) in dilute aqueous HCl, pH 5.0, with 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide, followed by exhaustive dialysis against aqueous 10 mM phosphate, 150 mM NaCl buffer, pH 7.4. Quantitation of the hapten/carrier ratio afforded ratios in the range 15:1. BALB/c mice were immunized with the KLH-phosphonate conjugate emulsified in complete Freund's adjuvant. A fusion with Sp2/0 myeloma as the fusion partner was performed by the standard methods,[1] and 13 IgG's were purified from ascitic fluid by affinity chromatography on protein A-coupled Sepharose 4B[1] and dialyzed exhaustively against reaction buffer (20 mM Tris·HCl, 20 mM NaCl, pH 8.5). The homogeneity of antibodies was determined by HPLC.[19]

The rates of hydrolysis of phenylacetate **2** in the presence (k_{obsd}) and absence (k_{uncat}) of antibody were determined at 35 °C, pH 8.5.[20] Of the 13 antibodies isolated, five (38%) were found to be catalytic. Lineweaver-Burke analyses of the antibody-catalyzed reactions afforded values of k_{cat} between 0.3 and 18.8 min^{-1} and K_m values between 157 and 534 μM. The fact that a high percentage of those antibodies isolated were catalytic may reflect that the tetrahedral phosphonate is a dominant structural and recognition element of this simple hapten. The IgG 20G9 has a k_{cat} of 18.8 min^{-1} and a K_m of 157 μM, which corresponds to a rate constant enhancement factor of 14 700 over the uncatalyzed reaction.[20] A K_i of 39 nM for phosphonate **1** was determined from Henderson plots[21] at 60 and 168 μM **2** for this antibody.

Antibody-containing micellar solutions were formed by injecting an aqueous antibody stock solution into an isooctane solution of 50 mM bis(2-ethylhexyl)sodium sulfosuccinate (AOT)/water.[23] Antibody-catalyzed hydrolysis of **2** by the antibody 20G9 was observed at Wo values between 21 and 31 (Figure 1), which is consistent with the Wo values forming the highest concentrations of reverse micelles as judged by UV absorbance. At a Wo of 23, Lineweaver-Burke analysis of the 20G9-catalyzed reaction afforded a k_{cat} of 3.89 min^{-1} and a K_m of 569 μM. While these results demonstrate retention of antibody activity in an isooctane bulk solution, detailed comparisons of catalytic rates in aqueous buffer and reverse micelles are complicated by the unknown pH and substrate concentrations inside the micelles. The changes in K_m and k_{cat} may also reflect the increased solubility of phenylacetate in isooctane relative to water (partition coefficient is 7), resistance to mass transfer across micellar boundaries, and/or possible changes in antibody structure within reverse micelles. Interestingly, spontaneous hydrolysis of phenylacetate **2** was not observed in reverse micelles containing buffer, a noncatalytic antibody, or hapten-inhibited catalytic antibody.

In conclusion, we have demonstrated that a catalytic antibody retains activity when solubilized within reverse micelles. Optimal antibody activity was observed at a Wo value of 28, consistent with the increased molecular weight of IgG molecules. Because the structures of antibodies are highly conserved, it is likely that most catalytic antibodies will also be active in reverse micelles. The ability of antibodies to function in reverse micelles should significantly expand the versatility of antibodies in catalysis.

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(18) Methyl 5-bromovalerate and triethylphosphite were heated to reflux for 14 h, and the resulting product was distilled to afford the phosphonate triester. The ester was hydrolyzed with concentrated HCl (100 °C), concentrated in vacuo, and converted to the acid chloride by treatment with thionyl chloride at reflux. The acid chloride was purified by distillation and subsequently converted to the phenyl triester by treatment with phenol (150 °C, 4 h). The ester was chromatographed on silica gel (Merck 60, 7:3 ether/hexanes) and subsequently hydrolyzed with 0.1 M aqueous NaOH (100 °C, 12 h). The reaction mixture was cooled, neutralized, applied to a DEAE-Sephadex column (HCO_3^- form), and eluted with a linear gradient of 0.0-1.0 M triethylammonium bicarbonate, pH 7.8. The phenylphosphonic acid was concentrated in vacuo, applied to a Dowex 50 (Li^+ form) column, and eluted with water to afford analytically pure hapten.

(19) Antibody was eluted from an ABX column (7.75 × 100 mm; J. T. Baker) with a linear gradient of 25 mM (2-[*N*-morpholino]ethanesulfonate (pH 5.7) to 1.0 M sodium acetate (pH 7.0) at 1.0 mL/min over 30 min.

(20) Initial rates were determined spectroscopically (270 nm) at pH 8.5 and 35 °C. Reactions were initiated by adding 50 μL of a 8.6 μM antibody stock solution to 1000 μL reaction buffer. Substrate concentrations (1% DMF final concentration) were determined spectroscopically (264 nm) and ranged from 42 μM to 1.40 mM. The uncatalyzed rate was determined between 5 and 40 mM Tris·HCl buffer concentrations (pH 8.5, 35 °C) and extrapolated to zero Tris·HCl, affording a value of k_{un} of 1.28×10^{-3} min^{-1}. Protein concentrations were determined via bicinchoninic acid method[22] and compared to a standard bovine IgG solution.

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(23) Antibodies were solubilized in micelles by either (a) adding 3.5 μL of a 185 μM stock antibody solution (20 mM NaCl, 20 mM Tris·HCl, pH 8.5) to 1000 μL of an isooctane solution containing 280 uM **2**, 50 mM AOT, and the appropriate concentration of water to yield Wo values between 11 and 36 or (b) adding 10 μL of a 70 μM stock antibody solution to 1000 μL of an isooctane solution containing 10 μL of water, 50 mM AOT, and varying concentrations of substrate.

Heme Model Studies Related to Cytochrome P-450 Reactions: Preparation of Iron-Porphyrin Complexes with Carbenes Bearing a β-Oxygen Atom and Their Transformation into Iron-*N*-Alkylporphyrins and Iron-Metallacyclic Complexes

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Evidence has been presented during this last decade for the formation of iron-carbene and iron-σ-alkyl complexes during the oxidation or reduction of several substrates by cytochrome P-450.[1] Model porphyrin complexes containing these iron-carbon bonds have been prepared and completely characterized.[1,2] The intermediate formation of such complexes has been recently postulated to interpret the hydrogen-deuterium exchange observed during *trans*-1-D-propene epoxidation by a rabbit liver cytochrome P-450 (Scheme I).[3]

Metallacyclic species of type A have also been proposed as possible intermediates in the formation of Fe—O—C—C—N *N*-alkylporphyrins of type C during oxidation of terminal alkenes by cytochrome P-450 and heme models.[4] The mechanism postulated in Scheme I involves the β-hydroxy-carbene complex B as a key intermediate that can form σ-alkyl complex A by intramolecular protonation at the carbenic carbon in a reversible process. These reactions have so far no precedent in the iron-porphyrin chemistry and raise several questions: (i) is it possible to prepare porphyrin-iron-carbene complexes with an oxygen atom in the β-position? (ii) are they transformed into σ-alkyl complexes by protonation? and (iii) do they lead to Fe—O—C—C—N

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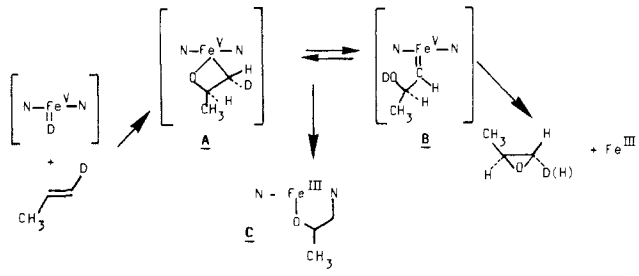
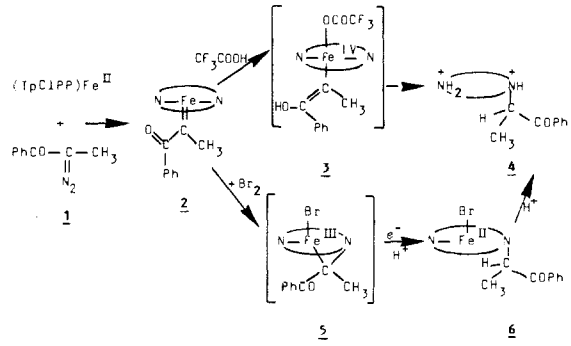
Scheme I



Scheme II

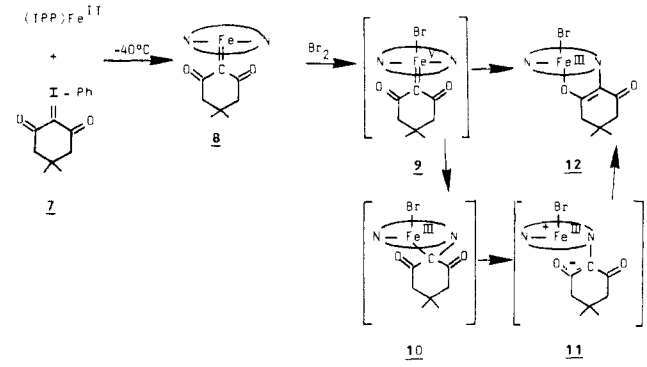


metallacyclic complexes?

This paper reports the first preparation of porphyrin–iron–α-ketocarbene complexes which contain an oxygen atom in the β-position of the carbenic carbon, upon reaction of Fe(II)-porphyrins with iodonium ylids or diazoketones, as well as some properties of these complexes.

Two types of precursors of α-ketocarbenes, the diazoketone **1**[5] and the iodonium ylid **7**,[6] were found to react with Fe(II) porphyrins leading to an almost quantitative formation of the iron–carbene complexes **2** and **8**. Complex **2** was prepared by reaction of 10 equiv of **1** with Fe^{II}(TpClPP)[7] in CH_2Cl_2 at room temperature under argon and exhibited UV–vis (411, 520, and 545 nm) and ^1H NMR data (8.48 ppm, 8 H, s, pyrroles; 7.92, 4 H, 7.79, 4 H and 7.64, 8 H, meso-phenyls; 7.05, 6.65, and 4.45 phenyl ligand, and −2.48, 3 H, s, CH_3) which were characteristic of diamagnetic low-spin (TpClPP)Fe^{II}–carbene complexes.[8] These spectroscopic data as well as the elemental analysis (C, H, N, Cl) and mass spectrum (m/e = 937, $M^+ - 1$, 10%; 806, Fe(TpClPP), 100%) of **2** were in complete agreement with the structure indicated in Scheme II. Complex **2** was stable at room temperature in deaerated CH_2Cl_2 but was transformed within a few minutes and almost quantitatively into the protonated *N*-alkylporphyrin **4** upon addition of a few equivalents of dry and deaerated CF_3CO_2H (Scheme II). Oxidation of **2** by 10 equiv of Br_2 in CH_2Cl_2 at −40 °C in the presence of sodium dithionite led rapidly to the iron(II)–*N*-alkylporphyrin complex **6** (yield about 50%) as shown by its characteristic UV–vis spectrum (455, 468 sh, 574, 619, 676 nm) which gave **4** upon acidic demetalation. Compound **4** was isolated from the reaction of **2** with CF_3COOH, transformed into its $Zn^{II}Cl$ complex, and completely characterized by UV–vis and ^1H NMR spectroscopy, mass spectrometry, and elemental analysis (C, H, N).[9]

Scheme III



Formation of **4** by reaction of **2** (formally a Fe^{IV}=C(CH_3)-COPh complex) with CF_3COOH could be due to a protonation of its Fe=C—C=O moiety leading to the σ-vinyl-Fe(IV) complex **3** whose analogues are well known to undergo migration of the σ-ligand to a pyrrole nitrogen[10] with formation of a complex of type **6**. This Fe(II) complex should readily demetalate in the presence of CF_3COOH in excess leading eventually to **4**. Formation of **6** upon oxidation of **2** by Br_2 could be explained by analogy to what was shown for the oxidation of the vinylidene carbene complex (TPP)Fe=C=C(pClC_6H_4)$_2$[11] with the involvement of the bridged carbene complex **5** which would be less stable than that derived from (TPP)Fe=C=C(pClC_6H_4)$_2$, its iron–carbon bond being more easily protonated to give a ferric complex of **4**. As our reactions were performed in the presence of dithionite, this ferric complex should be reduced very rapidly to the more stable ferrous complex **6**. In fact, satisfactory yields for Br_2 oxidation of **2** into **6** were only obtained in the presence of dithionite. This result is consistent with the instability of ferric complexes of *N*-alkylporphyrins[12] and the relative stability of the corresponding ferrous complexes.

Reaction of Fe^{II}(TPP)[7] with 2 equiv of **7** in CD_2Cl_2 at −40 °C quantitatively led to complex **8** which exhibited UV–vis (414, 512, and 538 nm) and ^1H NMR data in complete agreement with a diamagnetic Fe(II)–carbene structure (in particular, one singlet for H_{pyrr} at 8.51 ppm and two singlets at −0.06 and −1.08 for the CH_3 and CH_2 protons of the carbene ligand). Complex **8** was stable only below −30 °C. Its reactions with different acids such as HCl or CF_3COOH at −40 °C only led to the formation of Fe(TPP)(X). However, its treatment by 2 equiv of Br_2 in CH_2Cl_2 at −40 °C led to the formation of the metallacyclic complex **12** (30%) which exhibited, after purification, a ^1H NMR spectrum identical with that of an authentic sample prepared as described previously.[13]

Coming back to the questions raised in the introduction, the aforementioned results provide the following answers. First, porphyriniron–α-ketocarbene complexes can be prepared by two new techniques with either a diazoketone or an iodonium ylid. Second, these complexes exhibit a great propensity to undergo a migration of their carbene moiety to a pyrrole nitrogen. This may occur by simple protonation as in the case of complex **2**, presumably via a σ-alkyl–Fe(IV) intermediate (Scheme II). This reaction is the first indirect evidence for the passage from an iron–carbene to an iron–σ-alkyl complex by protonation.[14] Third,

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(9) m/e 983 (35%, $M^+ - 1$), 949 (20%, $M^+ - Cl$), 814 (100%, Zn(TpClPP)); ^1H NMR ($CDCl_3$) pyrrole H, 8.98 (1 H), 8.7 (1 H), 8.87 (1 H), 8.82 (1 H), 8.87 (1 H), 8.84 (1 H), 8.42 (1 H), 7.97 (1 H), (4 AB systems J = 4.5); *o*-phenyl H 8.3 (1 H, d, J = 7.5), 8.06 (1 H, d, J = 7.5), 8.15 (2 H, d, J = 7.5), 7.62 (2 H, d, J = 7.5), 7.7–7.85 (2 H); *m*-phenyl H 7.93 (4 H, d, J = 7.5), 7.7–7.85 (4 H); chain H −2.15 (1 H, q, J = 6), −3.3 (3 H, d, J = 6), 5.82 (2 H, d, J = 7.5), 6.78 (2 H, t, J = 7.5), 7.15 (1 H, t, J = 7.5).
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oxidation of carbene complexes **2** and **8** also leads to iron-*N*-alkylporphyrins, the formation of **12** from **8** giving a first example of passage from a carbene to a Fe—O—C—C—N metallacyclic complex. These reactions could occur via high-valent intermediates, formally Fe(V)=CRR′ complexes, such as **9**. A priori there are two possible evolutions of these complexes. The first one (a) could be a reductive elimination leading to ferric bridged carbene complexes such as **5** or **10** followed by a heterolytic cleavage of their Fe–C bonds. The derived enolate anion (such as **11**) should be more stable in the case of **11**[16] and more prone to form a Fe–O bond to give **12**. In that regard, it is noteworthy that the Zn(II) complex of **4** exists as a nonmetallacyclic β-keto-*N*-alkylporphyrin.[9] The second possible evolution (b) could be an isomerization leading to four-membered metallacyclic intermediates analogous to A followed by migration of the σ ligand to a pyrrole nitrogen giving eventually five-membered metallacyclic complexes such as C or **12**. Mechanism (b) should have led from **2** to a metallacyclic complex analogous to **12** but not to **6** as it was found. However, it is still difficult to conclude between paths (a) and (b) as we do not know the relative stabilities, under the reaction conditions, of **12** and of the corresponding metallacyclic complex which could be derived from **2**.

Finally, formation of **2** from a diazocompound and its transformation into a *N*-alkylporphyrin are first evidences for reactions recently postulated for *N*-vinylheme formation upon cytochrome P-450-dependent oxidation of a sydnone.[15]

(14) A recent result[11c] describing the passage from the vinylidene complex Fe[TPP][C=C(pClC$_6$H$_4$)$_2$] to N—CH=C(pClC$_6$H$_4$)$_2$TPPH by acidic treatment could be also interpreted by a similar mechanism involving a Fe(IV) intermediate.

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The Use of Alkoxy-Substituted Anomeric Radicals for the Construction of β-Glycosides

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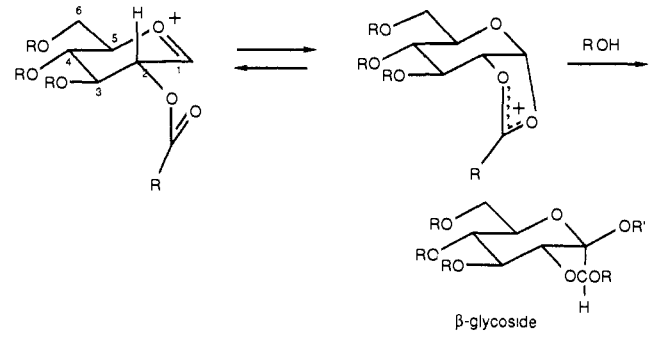
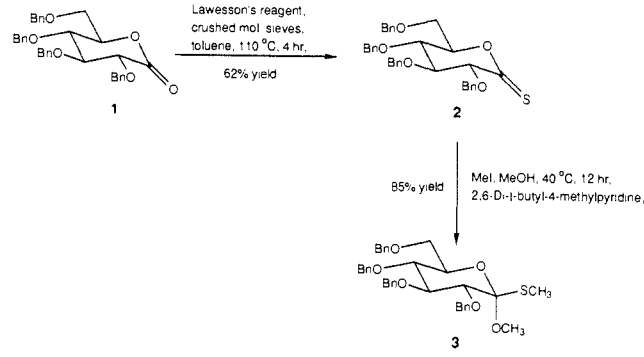
The construction of β-glycosides has been a long standing problem in oligosaccharide synthesis.[1] Most of the methods developed to date rely on S_N2 displacement of glycosyl halides at the anomeric carbon and apply only to a limited set of substrates. For instance, while β-linkages to sugar derivatives containing an equatorial C-2 acetoxy (or benzoyloxy) group can be made relatively easily (Scheme I),[2] it is extremely difficult to form β-linkages to many other sugars, including mannose and rhamnose derivatives (where the C-2 hydroxyl is axial) and all 2-deoxy sugars.[3] Because many biologically important oligosaccharides contain β-linkages to these sugars,[4] more general strategies are necessary. Preliminary results on a radically new method for constructing β-glycosides are presented below.

Scheme I



Scheme II



The method relies on generating an alkoxy-substituted radical at the anomeric carbon of a sugar. Previous work has shown that hydrogen atoms delivered to unsubstituted anomeric sugar radicals end up axial in the products, suggesting the anomeric radicals prefer to be axial in order to maximize overlap with the lone pair of the ring ether oxygen.[5] However, the corresponding alkoxy-substituted sugar radicals have never been studied.[6] We recognized that if the hydrogen still ended up axial when an alkoxy substituent was present, the product would be a β-glycoside.

A priori it is difficult to predict the stereochemical outcome in such a case because anomeric alkoxy substituents also prefer to be axial.[7] However, the question is not simply whether the radical or the alkoxy group is more stabilized by orbital overlap with the ring oxygen, because the exocyclic alkoxy group may also help stabilize the radical. Moreover, it is not clear to what extent hydrogen atom delivery to such a system is affected by steric interactions. To complicate matters further, recent ESR studies show that anomeric radicals in sugars can exist in either a boat, chair, or half chair conformation depending on the structure of the parent carbohydrate.[8] It is not known what effect, if any,

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