Metalloporphyrins in Oxidative Catalysis. Oxygen Transfer Reactions of Oxochromium Porphyrins

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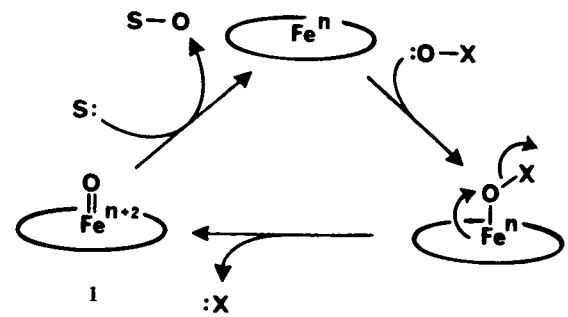
Abstract. The oxidation of chloro-5-10,15,20-tetramesitylporphyrinotoiron(III) with peroxyacids affords a reactive oxoiron(IV)-porphyrin cation radical species **2**. The characterization of **2** and its oxochromium analogs **3**, **4** and **5** are reviewed. The nature of reactive oxochromium species derived from chromyl reagents is also reviewed. The oxidation of triphenylphosphine by CrOTPP (**11**), CrOTTP (**13**) and CrOTMP (**14**) is described. Variations in the rate constants indicate that steric factors affect the rate of oxygen atom transfer. Activation parameters for the oxidation of triphenylphosphine by **14** are $\Delta H^{\neq}$ = 6.96 kcal/mol and $\Delta S^{\neq}$ = −39 eu. The oxidation of *t*-butylphenylcarbinol (**18**) by CrOTPP gave predominantly benzaldehyde via carbon–carbon bond cleavage while the chromium(III) porphyrin-catalyzed oxidation of **18** by iodosylbenzene afforded *t*-butylphenylketone.

INTRODUCTION

The variety of oxidations mediated by the heme-containing monooxygenase, cytochrome P-450, and the relationship of these transformations to both endogenous and xenobiotic metabolism has focussed sustained attention on the mechanism of action of this enzyme for more than twenty years [1]. The ability of this enzyme to function in the presence of exogenous oxygen donors such as alkyl hydroperoxides and iodosylbenzene [2] has suggested mechanistic similarities to the peroxidases for which oxoiron(IV) and oxoiron(V) equivalents are isolable intermediates [3]. A useful chemical simplification of the processes of oxygen transfer by iron is the *oxygen rebound mechanism* (Scheme 1) [4]. Heterolytic cleavage of the O–X bond of a typical peroxidic oxygen donor at a metal center can lead to a reactive metal-oxo intermediate (**1**) which is able to transfer its oxo ligand to the organic substrate molecule.

The isolation and characterization of simple synthetic oxometalloporphyrins has provided a rationale for these enzymic processes [5b]. Further, the demonstration that iron porphyrin complexes are capable of catalytic oxygen transfer to hydrocarbons with iodosylbenzene as an oxygen donor [5] has provided the impetus for a large number of porphyrin-based catalytic systems for oxygen transfer based on this biochemical analogy [6]. The sterically hindered 5,10,15,20-tetramesitylporphyrinatoiron complex has been shown to produce an unusually stable oxidized species upon reaction with a variety of oxidants. Thus, the oxidation of this complex with *m*-chloroperoxybenzoic acid at −78°C has been shown to produce a green species **2** [7]. Several lines of evidence now support the formulation of **2** as an oxoiron(IV) porphyrin cation radical formally equivalent to the



Scheme 1.

celebrated compound I of horseradish peroxidase. The visible spectrum of **2** shows the characteristic long-wave length absorption of a porphyrin radical. Further, large downfield shifts for the aryl hydrogens in the proton NMR spectrum of **2** (δ 68 (m H); 24 and 26 (*o*-methyl); 11.1 (*p*-methyl)) are also indicative of substantial spin and charge density on the porphyrin ring. The isomer shift in the iron Mössbauer spectrum of **2** (δ 0.06) is in the range of other iron(IV) complexes. The complicated magnetic field and temperature dependence of the Mössbauer data are closely modelled by an $S = 1$ iron(IV) coupled strongly and isotropically to the $S = 1/2$ porphyrin [8a]. Magnetic moment measurements and the EPR spectrum were also consistent with a 3/2 spin system for **2** [9]. Recent EXAFS data have provided evidence that the iron-oxygen distance in **2** is 1.6 Å [8b].

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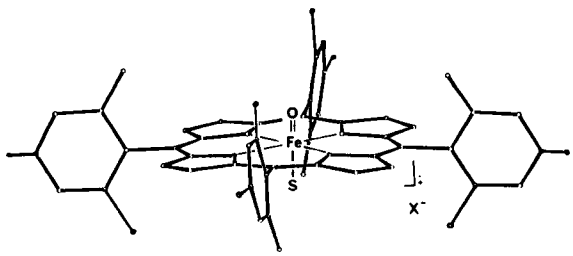
Abbreviations. TPP, 5,10,15,20-tetraphenylporphyrin; TTP, 5,10,15,20-tetra(p-tolyl)porphyrin; TMP, 5,10,15,20-tetramesitylporphyrin.



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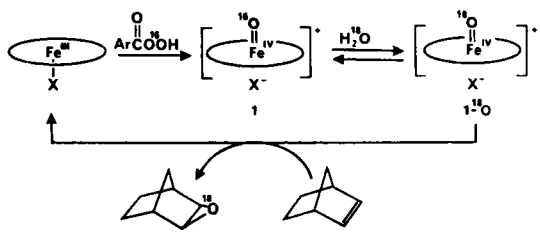
The high chemical reactivity of 2 toward hydrocarbons has indicated that it is kinetically competent to be the reactive species in the iron porphyrin catalytic systems. That the O–O bond is broken in the reactive complex is supported by the efficient incorporation of ^{18}O into the product epoxide in the presence of olefinic substrates. Peroxyacids do not exchange the peroxidic oxygen with water whereas the oxo ligand of metaloxo complexes do [10]. Thus, a mechanism for oxygen transfer to olefins via 2 is that shown in Scheme 2.



Scheme 2.

In contrast to the porphyrin radical character of 2, the two-electron oxidation of chromium(III) porphyrins has been shown to produce a species with a simple room temperature EPR spectrum characteristic of chromium(V) [11]. That the oxidation of CrTPP(Cl) with iodosylbenzene produced an oxochromium(V) complex (3) was supported by the stoichiometric epoxidation of norbornene and the observation of a chromium-oxygen stretching band in the infrared spectrum at 972 cm^{-1} [12]. Further evidence for the structure of 3 derives from its facile reduction to the stable, isolable oxochromium(IV) complex 4. Suitable single crystals of the tetra(*p*-tolyl) derivative 5 have allowed the assignment of the crystal and molecular structure of 5 to be that shown in Fig. 1 [12]. A stable, isostructural chromium(V) nitride has also been fully characterized [13].

The mechanisms of hydrocarbon oxidation by chromyl reagents have been investigated for some time. The oxidation of aryl methanes was observed to proceed with a large isotope effect (k_H/k_D = 6.4): a negative Hammett ρ-value of −1.4 and a hydrogen selectivity similar to that of bromine atoms [14]. These results are best accommodated by the hydrogen atom abstraction–recombination mechanism suggested by Wiberg [15]. The retention of configuration observed in some cases requires the recombination process to be very rapid.

The oxidation of alcohols by the chromium(VI)-hydroxy-acid complex 6 has been shown to involve two distinct processes: a two-electron reduction of Cr(VI) to Cr(IV) with concomitant oxidation of the alcohol and a subsequent one-electron, oxidative decarboxylation to give chromium(III) [16]. These results have confirmed earlier indications that Cr(IV) is a selective one-electron oxidant whereas two-electron processes are favored with Cr(VI).

There is increasing evidence that chromium(V) complexes are more generally involved in the oxidations of organic compounds by chromyl reagents than has previously been supposed. The reaction of chromyl chloride with phosphorus pentachloride has been

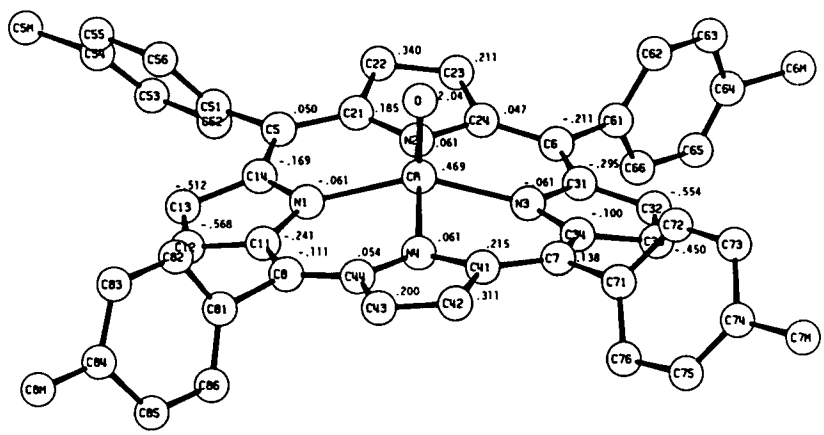
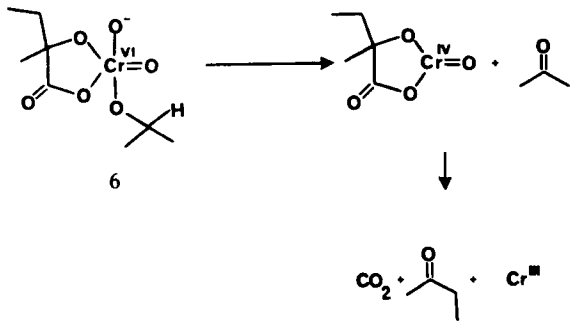


Fig. 1. Molecular structure of CrOTTP, 5. Superscripted numbers show vertical deviations in Å from the plane of the four pyrrole nitrogens.



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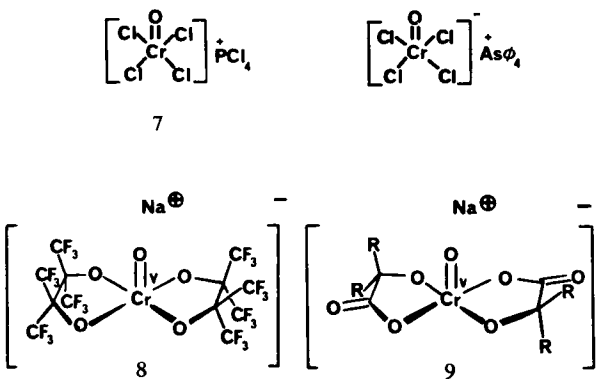
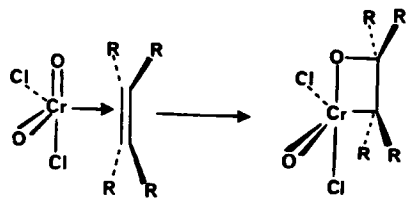
shown to produce an oxotetrachlorochromate(V) anion (7). The X-ray structure of the tetraphenylarsenium derivative of 7 has been reported [17]. Several reports have appeared describing EPR signals attributable to chromate(V) species with g-values near 1.97 [18]. Stable, oxochromate(V) ions **8** and **9** have also been described. Probably due to the anionic nature of these species, they are apparently not powerful oxidants [19].



7 8 9

The mechanism of olefin epoxidation by oxochromium compounds has received considerable recent attention. Involvement of the metal to form an intermediate oxametallacycle **10**, originally proposed by Sharpless on the basis of product stereochemistry [20], has been supported by the results of general valence bond calculations [21] and gas phase SIFT techniques [22].



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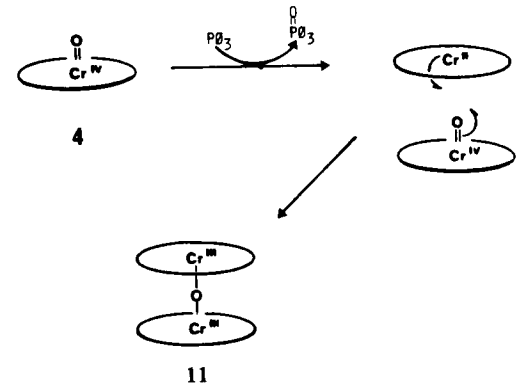
Kochi has demonstrated that the stoichiometrically significant oxidant in reactions of chromyl compounds may be critically dependent upon solvent [23]. Thus, while chromium(VI) appears to react with olefins and alcohols directly in methylene chloride, solvents such as pyridine or DMF caused rapid reduction of chromyl nitrate to an oxochromium(V) intermediate which was shown to be responsible for substrate oxidation.

RESULTS AND DISCUSSION

Oxygen Transfer from Oxochromium(IV) Porphyrins. The Reaction with Triphenylphosphine

Whereas oxochromium(IV) porphyrins are unreactive toward hydrocarbons, we have shown that triphenylphosphine reacted with CrOTPP (**4**) to give triphenylphosphine oxide [12]. The transfer of oxygen to triphenylphosphine by bisoxomolybdenum(VI) porphyrin [24] and oxoiron(IV) porphyrins [25] has also been reported. In benzene solution concomitant formation of a dimer (μ-O) $(CrTPP)_2$ (**11**) indicated the reduction of **4** to Cr(II)TPP and subsequent coupling to form **11** (Scheme 3). The clean production of CrTPP(Cl) in methylene chloride suggested a rapid reaction of Cr(II)TPP with the halogenated solvent, as expected for chromium(II).



4 11

Scheme 3.

Visible spectral changes for the reaction of CrOTPP with triphenylphosphine in methylene chloride are shown in Fig. 2. Under pseudo-first order conditions of high phosphine concentrations, good kinetic data were obtained over two to six half-lives for CrOTPP, CrOTTP (**5**) and CrOTMP (**12**). A plot of the time course for the reaction with CrOTMP is shown in Fig. 3 and kinetic data for the three oxochromium(IV) complexes are presented in Table 1.

Table 1. Oxidation of Triphenylphosphine by Oxochromium(IV) Porphyrins

Porphyrin	Rate[a]	Correlation Coefficient[b] (r)
CrOTPP (4)	0.47 M^{-1} s^{-1}	0.9993
CrOTTP(5)	0.37 M^{-1} s^{-1}	0.9993
CrOTMP (12)	0.054 M^{-1} s^{-1}	0.9996
cis-MoO_2TTP[c]	0.07 M^{-1} s^{-1}	

a. Bimolecular reaction rate in methylene chloride at 25°.
b. Based on least-squares analysis through at least four $\tau_{1/2}$.
c. Reaction in benzene at 20°C (cf. Ref. 24b).

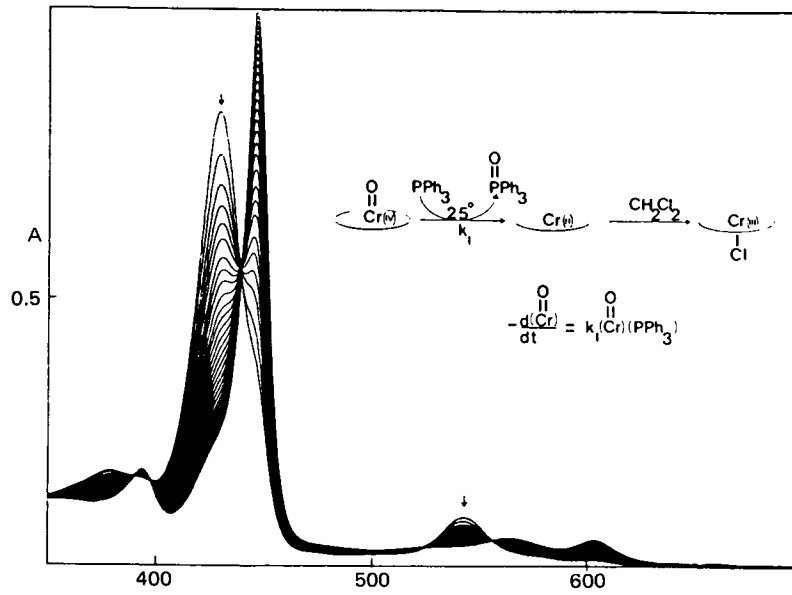


Fig. 2. Visible spectral changes during the reaction of CrOTPP (4) with triphenylphosphine at 25° in methylene chloride.

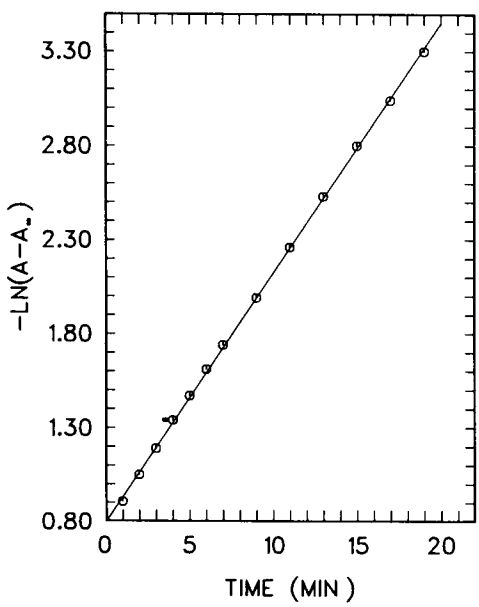


Fig. 3. Pseudo-first order plot of the reaction of CrOTMP (12) (7.2×10^{-6} M) with triphenylphosphine (3.19×10^{-3} M) in methylene chloride at 25°.

An Arrhenius plot for the reaction of CrOTMP with triphenylphosphine from 5 to −15° revealed a low $\Delta H^{\neq}$ (6.96 kcal/mol) and a large negative entropy term (−39 eu) (Fig. 4). Since solvation changes are unlikely to be a large contributor in methylene chloride, the transition state for this oxygen transfer reaction must be highly ordered. Interestingly, the ^{18}O-exchange of $[MoOCl_5]^{2-}$ with water in HCl for which a dimeric intermediate has been suggested also proceeds with a significant negative entropy of activation (−18.7 eu).

Since both reactants are diamagnetic and the initially formed chromium(II) is paramagnetic, a concerted oxygen transfer is not a likely mechanism. An associative pathway via the phosphorus radical adduct **13** is consistent with the activation parameters, the known autoxidation reaction of phosphines and the electron-spin imposed requirement for an intermediate in this reaction.

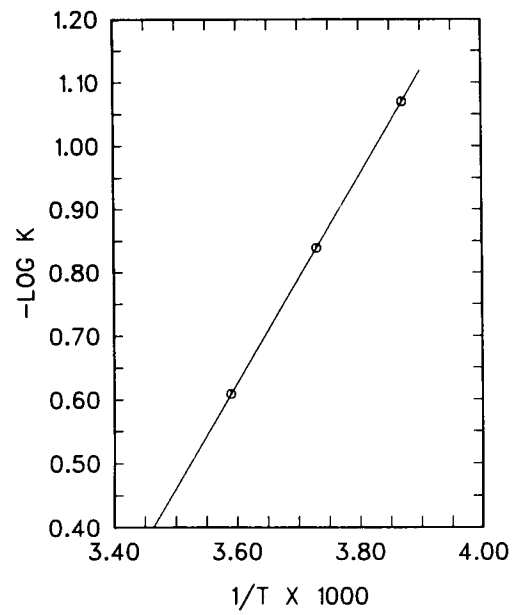
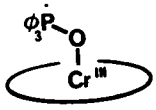


Fig. 4. Arrhenius plot for the reaction of CrOTMP (12) with triphenylphosphine in methylene chloride.

The pronounced effect of the ortho-methyl groups of CrOTMP observed here for the transfer of oxygen to phosphorus is further evidence of the importance of stereoelectronic effects in the reactivity of oxometalloporphyrin complexes [26]. Consideration of the orbital symmetries of the chromyl bond leads to the expectation that an approaching nucleophile will interact with the chromium-oxygen *antibonding* orbital as in **14**. To initiate bonding with the oxo-ligand the phosphorus lone pair must avoid interactions with the oxygen lone pair and the metal *d*-orbital. Such orbital symmetry considerations cannot preclude the subsequent formation of a cyclic species such as **15**, however [27].



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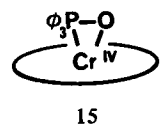

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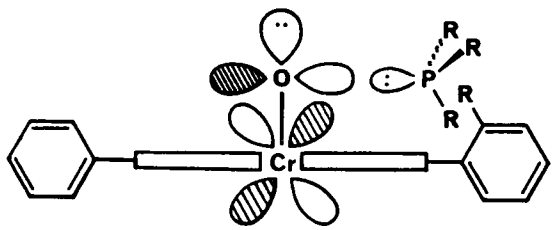

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Alcohol Oxidation by Chromium(IV) and Chromium(V)

That chromyl reagents evolved reactive chromium(IV) and chromium(V) intermediates was originally suggested on the basis of reactivity patterns [14,16]. Thus, cyclobutanol and *t*-butylphenylcarbinol have been shown to be oxidized to ketones by chromium(V) whereas C–C bond cleavage products resulted from the reactions with chromium(IV) species. We have found that these reactivity patterns persist with the oxochromium porphyrin complexes.

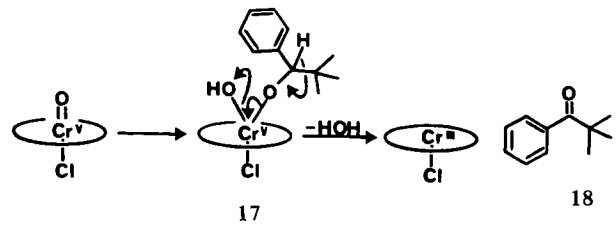
Table 2. Alcohol Oxidations Promoted by CrOTPP and CrTPPCl/Iodosylbenzene in Methylene Chloride

Porphyrin/Oxidant	Substrate	Product	Yield
CrOTPP[a]	16	17/18=10	80%
CrTPPCl/iodosylbenzene[b]	16	17/18=0.48	44%
CrTPPCl	16	–	0
MnO_2[c]	16	18	100%
CrOTPP[a]	benzyl alcohol	17	100%
CrTPPCl/iodosylbenzene	benzyl alcohol	17	56%

a. This reaction was carried out in a sealed tube at 70°C in Argon purged with methylene chloride.
b. Yield relative to oxidant after six turnovers.
c. Ten-fold molar excess of activated manganese dioxide.

The reaction of CrOTPP (**4**) in methylene chloride with *t*-butylphenylcarbinol (**16**) at 70°C afforded benzaldehyde (**17**) in 73% yield. Small amounts of *t*-butylphenylketone (**18**) (<7%) were also produced (Table 2). Neither *t*-butyl chloride nor *t*-butanol were produced, and CrTPP(Cl) was ineffective in promoting this oxidation. By contrast catalytic reactions involving CrTPP(Cl) and iodosylbenzene resulted in predominate production of *t*-butylphenyl ketone (2.1:1 relative to benzaldehyde). Iodosylbenzene did not function as a viable oxidant under the conditions of this experiment when catalyst was absent.

These results are consistent with a two-electron oxidation by the oxochromium(V) complex to give *t*-butylphenylketone and an one-electron cleavage reaction by the oxochromium(IV) species. The small amount of ketone observed in the CrOTPP stoichiometric oxidation of **16** may have evolved from disproportionation of CrOTPP to chromium(V) and chromium(III) [28]. The appearance of some cleavage products in the catalytically promoted oxidation cannot be due to the formation of CrOTPP since this oxidant is unreactive at 25°C. A more reasonable explanation for this result is that there is more than one mechanism available for alcohol oxidation by chromium(V). The rapid exchange of the oxo-ligand in **16** with $H_2^{18}O$[6] suggests an alkoxychromium(V) intermediate (**17**). Homolysis of the C–C bond in **17** would lead to benzaldehyde and chromium(IV) whereas cleavage of the C–H bond would generate the ketone. Thus, as with the intermediates generated from other chromyl reagents, CrOTPP functions as a one-electron oxidant, whereas the CrTPPCl/iodosylbenzene couple via the oxochromium(V) complex oxidizes primarily by the two-electron pathway.



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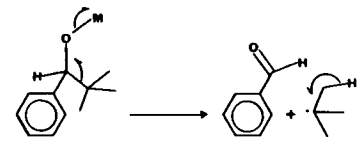

EXPERIMENTAL

General

Analytical VPC was conducted using either a Varian 1200 or Varian 3700 gas chromatograph. Component identification was established using co-injection with authentic samples and comparative mass spectral analysis on a Finnigan 4000 GC/MS. Reaction quantitation was performed by VPC using an internal standards method employing either a Spectra Physics SP 4100 computing integrator or a Hewlett-Packard 3380A electronic

integrator. Visible spectra were obtained on either a Cary-14 or a Varian-Cary 219 spectrophotometer. Chromium porphyrins were prepared as we have reported elsewhere [26,28].

Kinetics of Triphenylphosphine Oxidation by CrOTMP 12, CrOTPP 4 and CrOTTP 5 in Methylene Chloride

Pseudo first-order rate constants for the oxidation of triphenylphosphine by chromium(IV) species were determined by using large concentrations ($10-10^4$ fold excess) of triphenylphosphine relative to metalloporphyrinate. The rate of reaction was determined by monitoring the appearance of CrTMPCl (609.5 nm), CrTTPCl (605 nm) and CrTPPCl (603.5 nm).- CrOTTP and CrOTPP showed linearity in the plot of log $(A-A_\alpha)$ vs. time over two or three half lives while for CrOTMP linearity was maintained throughout for six half lives. The absorbance at infinity (A_α) was determined by allowing each reaction to exceed seven half lives.

In a typical determination, CrOTMP (5.85 mg, 6.89 μmol) was dissolved in 100 ml of potassium carbonate-treated methylene chloride. A 2-ml aliquot was diluted to 25 ml (5.51×10^{-6} M) and 2 ml of this solution was added to a cuvette equipped with a teflon stopper with no provision to exclude oxygen. Recrystallized triphenylphosphine (340 mg, 1.30 mmol) was dissolved in 1 ml of methylene chloride, and 100 μl of this solution was syringed into the cuvette (6.19×10^{-2} M in triphenylphosphine) which had been maintained at 24.6 ± 0.1°. Absorbance at 609.5 nm was monitored and recorded each minute in the wavelength/time mode. The absorbance at infinity ($A_\alpha = 1.023$) was obtained within 30 min, and the data were collected over five half lives ($k = 0.168$ min^{-1}, $r = 0.998$ for 16 data).

Oxidation of t-Butylphenylcarbinol by CrOTPP (4)

CrOTPP (13.0 mg, 19.1 μmol) and purified *t*-butylphenylcarbinol (3.18 mg, 19.4 μmol) were added to a tapered 5 ml vial equipped with a teflon septum, two-way septum valve and stir bar. Nitrogen-purged methylene chloride (0.8 ml) was added, and the vial was purged with argon. The valve was closed, and the vial was heated in an oil bath (70–75°C) for 18 h.

Gas chromatographic analysis using added iodobenzene (2.3 μmol, 4.33 min) as an internal standard revealed benzaldehyde (7.2 μmol, 5.35 min), *t*-butylphenylketone (0.6 μmol, 7.95 min) and starting carbinol (11.2 μmol, 13.96 min) (10′ × 1/8″ 20% DEGS on 60/80 Chromosorb W at 160°C). The overall yield based on the conversion of chromium(IV) to chromium(III) was 80%. Neither *t*-butyl chloride nor *t*-butanol was produced. No reaction was observed under these conditions with CrTPPCl after 64 h.

Catalytic Oxidation of t-Butylphenylcarbinol Using CrTPPCl and Iodosylbenzene

Iodosylbenzene (54.0 mg, 243 μmol) was slowly added to a solution of CrTPPCl (30.0 mg, 42.8 μmol) and purified *t*-butylphenylcarbinol (140 mg, 243 μmol) in 5 ml of methylene chloride under the usual conditions. The addition of solid oxidant was carried out over a 20-min period. Cyclododecane (105 μmol, 3.06 min) was used as an internal standard, and the ratio of ketone to aldehyde was 2.1:1 in 31% yield relative to oxidant. The analysis was conducted as described in the preceding experiment. Iodosylbenzene alone caused negligible oxidation of *t*-butylphenylcarbinol under these conditions.

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