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PINACOL CLEAVAGE USING IRON(III)TRISPHENANTHROLINE COMPLEXES

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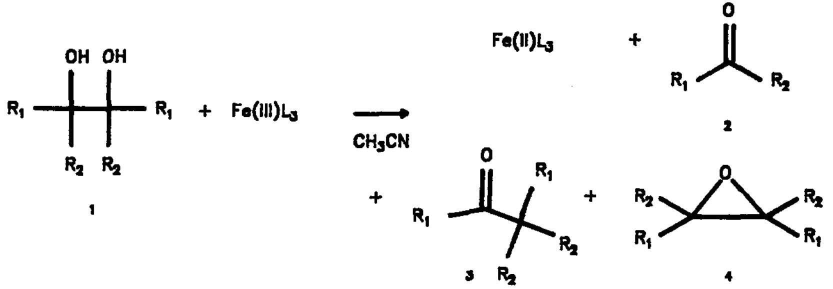
Summary: Oxidative bond cleavage of benzpinacol and 2,3-diphenyl-2,3-butanediol have been effected with two $Fe(III)(1,10\text{-phenanthroline})_3$ complexes which are thought to undergo electron transfer reactions by an outer sphere mechanism. The products of these reactions are exclusively the corresponding ketones when 2,6-di-*t*-butylpyridine is added to the solution. In contrast to the facile oxidations of these aromatic substrates, pinacol is not cleaved under these reaction conditions.

Recently, we have been interested in ways to enhance the cleavage of radical cation $C\text{-}C^{\cdot+}$ bonds. The $C\text{-}C^{\cdot+}$ bond cleavage is expected to occur with lower energy requirements (and therefore lower temperature requirements) than the corresponding C-C neutral species.[1-3] Since the formation of radical cation species necessarily requires the transfer of an electron from a C-C moiety to an appropriate electron acceptor, a detailed understanding of radical cation bond cleavage reactions can only be obtained if the details of the electron transfer process are well understood. As a prelude to a detailed mechanistic study of endoergic electron transfer rates, we required a bond cleavage reaction initiated by an electron transfer in which the products could be identified and completely characterized. Suitable candidates for such electron transfer processes were the $Fe(III)(1,10\text{-phenanthroline})_3$ complexes ($Fe(III)L_3$) which have previously been shown to undergo electron transfer processes by an outer sphere mechanism in the oxidation of a variety of alkyl metals.[4] These compounds are both strong[5] and tunable[7] oxidants, enabling reaction rates to be easily measured near ambient temperature. Pinacols were chosen to be the electron donors because the radical cations of **1a** and **1b** had previously been shown to undergo rapid bond cleavage.[1] Although pinacols are well known to undergo oxidative cleavage, all previous examples of this cleavage proceed *via* an inner sphere electron transfer[8] or radical chain processes.[9] We report here that appropriate pinacols can be cleaved by $Fe(III)L_3$ complexes by a homogeneous electron transfer process.

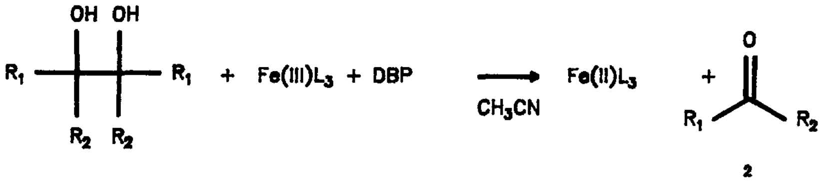
Reaction of 0.01 M acetonitrile solutions of pinacols **1a** and **1b** with either equimolar $Fe(III)L'_3(PF_6)_3$ or $Fe(III)L''_3(PF_6)_3$ proceed smoothly at room temperature to form a mixture of **2**, **3**, and **4** and the corresponding $Fe(II)L_3$ complex. The product structures were identified through GCMS, HPLC, and TLC analyses. The products from the reaction of **1a** were confirmed by mixed melting points with authentic samples. As the temperature of the reaction is increased, the reaction rate increases dramatically, with the reactions initiated by Fe(III)L'$_3$ being completed within 2 hours at 50°C. These results are shown in equation 1.



(1)

a) $R_1 = R_2 = Ph$ L' = (1,10-phenanthroline)
b) R_1= Me; R_2 = Ph L" = (4,7-diphenyl-1,10-phenanthroline)

The origin of each of these products is of interest. The mole % yield of products 3 and 4 are observed to increase with time. Analyses of the reaction mixtures at early time show little or no formation of these products. When 2,6-di-*t*-butylpyridine (DBP) is added to the reaction solution, the formation of 3 and 4 are completely suppressed. Since 3 and 4 have previously been shown to arise from an acid catalyzed pinacol rearrangement,[10] the presently observed formation of 3 and 4 at late times indicate that acid is being produced during the course of the reaction and is not present initially. Thus, the sole product of the Fe(III)L$_3$ induced bond cleavage reaction is ketone 2. This reaction is exactly analagous to previously reported oxidative cleavage reactions of glycols.[8,9,11,12]



(2)

a) $R_1 = R_2 = Ph$ L' = (1,10-phenanthroline)
b) R_1= Me; R_2 = Ph L" = (4,7-diphenyl-1,10-phenanthroline)

A test of the electron transfer nature of the reaction is provided by 2,3-dimethyl-2,3-butandiol, 1c. The absence of aromatic moieties would be expected to make this compound much less susceptible to oxidation by an electron transfer pathway,[13] while reaction pathways involving bond formation directly to the Fe center may still be feasible. Careful monitoring of both the disappearance of 1c by GLC analysis and the appearance of acetone by HPLC analysis allow us to conclude that <1% reaction occurs within 24 hours with either Fe(III)L'$_3$ or Fe(III)L"$_3$ as the electron acceptor. This is in sharp contrast to the reaction of 1a in which complete reaction is observed in the same time period.

(3)

Results of quantitative analyses of the reaction mixtures are gathered in Table 1. For **1a** and **1b**, the reacted pinacol can be accounted for quantitatively in products **2**, **3**, and **4**. When **DBP** is added to the solution, two moles of **2** are formed for each mole of **1** reacted. The stoichiometry of the formation of **2** is two moles of Fe(III) for each mole of either **1a** or **1b**, since only 50% conversion of **1** to **2** is obtained when using 1:1 molar ratios of Fe(III) and **1**.

Although the exact detailed mechanism of this electron transfer reaction cannot be determined at this time, the following facts indicate that the reaction is initiated by a rate-determining electron transfer from the pinacol to the Fe(III)L_3. The reaction is not acid catalyzed, since the addition of **DBP** to the solution results in the elimination of two products (*i.e.*, **3** and **4**) whose chemistry has been previously shown to result from acid catalysis.[10] The reaction is not base catalyzed, since uniform reaction rates are obtained upon the addition of a sufficient amount of **DBP**. Rate-determining homolytic bond cleavage of **1a** or **1b**, followed by a fast oxidation of the resulting radicals, may be ruled out by the observed reaction rate, since the homolytic bond cleavage energy of **1a** has previously been reported to be $\Delta G^{\ddagger}_{303} \approx$ 32.3 kcal/mole.[14] An outer sphere electron transfer in these bond cleavage reactions is suggested by the outer sphere behavior of Fe(III)L_3 with alkyl metals.[4] The cleavage reaction observed here is fundamentally different than the inner sphere oxidative cleavage initiated by Co(III)[8a] or other metals[12] which proceed at a much faster reaction rate even though Co(III) has a much lower reduction potential.[15] The facile cleavage of **1a** and **1b** coupled with the nonreactivity of **1c** indicate a crude correlation of the reaction rates with the oxidation potential of the pinacol in accord with the Marcus theory of outer sphere electron transfer.[16] Thus, the bond cleavage reactions of **1a** and **1b** must be initiated by an electron transfer from the pinacol to the Fe(III)L_3 complex.

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Table 1
Quantitative Analysis of Reaction Products

Starting Materials (0.01 M)			Product Yields (mole %)[a]					
	FeL_3	DBP (M)	2	3	4	Time (h)	Temp (°C)	conversion (%)
1a	L'	--	91	14	48	24	25	45
		--	146	5	26	2	50	41
		--	130	10	33	4	50	56
		0.005	190	--	--	2	50	36
	L"	0.005	189	--	--	2	50	18
		0.005	190	--	--	24	25	8.4
1b	L'	--	162	--[b]	--[b]	24	25	51
		--	203	--	--	1	50	33
		--	167	--[b]	--[b]	2	50	47
		0.005	200	--	--	2	50	44
	L"	0.005	190	--	--	2	50	24
		0.005	196	--	--	24	25	21
1c	L'	0.005	--	--	--	24	30	<1%
	L"	0.005	--	--	--	24	30	<1%

a) Yield data ± 5%, measured by HPLC on a reverse phase C-8 column using a uv detector (254 nm) and benzonitrile or phenyl benzoate as an internal standard.
b) Product observed, but the yield was not determined.

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