the calculated shifts are only about 25% of the observed shifts. Elimination of the discrepancies requires an unrealistically high dome angle, ~35°. Dome angles less than 19° produce corresponding smaller shifts. Perutz' estimate (0.75 Å)[2] of the iron-to-mean heme plane displacement in deoxyhemoglobin requires a dome angle of 19° if the Fe–N bond length is 2.086 Å as suggested[11] for high-spin Fe(II). In the single available high-spin Fe(II) porphyrin X-ray crystal structure,[11] both the displacement and the dome angle are somewhat lower, 0.55 Å and 7°, respectively. The significance of this difference is currently under debate.[11,12] In any event, it is most unlikely that the actual dome angle in deoxyhemoglobin is much larger than 19°.

We found that the observed shifts can be satisfactorily reproduced if, in the 19° domed structure, small alterations were made in the force field, consistent with Hückel molecular orbital calculations (to be published elsewhere) of the changes in π-bond order on doming, resulting from decreased π overlap at the methine bridges. These changes, amounting to 2–5%, were translated into force constant changes ($\Delta K_{C_\alpha C_\beta} = 0.1$, $\Delta K_{C_\alpha N} = 0.1$, $\Delta K_{C_\alpha C_m} = -0.2$, and $\Delta K_{C_\beta C_\beta} = -0.1$ mdyn/Å), using Gordy's relation.[13] In addition the $C_mC_\alpha N$ bending force constant was reduced by 0.2 mdyn/Å. No attempt was made to refine these force constant changes, and the similarity of the patterns of observed and calculated frequency shifts lends strong support to the view that spin-state effects on the resonance Raman spectra are largely the result of disruption of the porphyrin π conjugation brought about by doming.

It is of interest that the ~1375 cm^{-1} oxidation-state marker band[3b,15] is shifted to higher frequency by the kinematic effects of doming but to lower frequency by the change in force field. Thus its essential invariance (i.e., 1362 cm^{-1} in cytochrome c and 1358 cm^{-1} in deoxyhemoglobin) to changes in spin state appears to result from effective cancellation of kinematic and force-field effects. This mode, which produces the strongest Raman feature in resonance with the Soret band,[3b,16] had previously been assigned[3b,17] to C–N stretching. In fact it involves bonds in the outermost part of the porphyrin ring.

While further calculations are needed to explore alternative plausible force-field variations, it is encouraging that the preliminary calculations have yielded straightforward results: (1) a simple force field fits the porphyrin-ring frequencies with good accuracy; (2) the kinematic consequences of doming, while not negligible, are relatively small; (3) the frequency shifts associated with conversion of low-spin to high-spin heme proteins can be reproduced with force-field changes that are plausibly related to changes in electronic structure.

References and Notes

(1) This work was supported by NIH Grants HL-12526 and GM-13498 and by NSF Grant GP-41008X.

(2) M. F. Perutz, *Nature (London)*, **228**, 726 (1970).

(3) (a) T. G. Spiro and T. C. Strekas, *Proc. Nat. Acad. Sci. U.S.A.*, **69**, 2622 (1972); (b) *J. Am. Chem. Soc.*, **96**, 338 (1974).

(4) H. Ogoshi, Y. Saito, and K. Nakamoto, *J. Chem. Phys.*, **57**, 4194 (1972).

(5) (a) The coordinate symbols are the same as those defined in ref 4. (b) The iron atom was omitted in these preliminary calculations. Subsequently, the iron atom has been included in the calculation of planar OMP frequencies. The high-frequency modes discussed here remained essentially constant over a wide range of values for the FeN stretching force constant.

(6) L. J. Radonovich, A. Bloom, and J. L. Hoard, *J. Am. Chem. Soc.*, **94**, 2073 (1972).

(7) J. L. Hoard, *Science*, **175**, 1295 (1971).

(8) A fourth band, 1592 cm^{-1} (A_{1g}) in ferrocytochrome c, was originally thought to shift to 1565 cm^{-1} in deoxyhemoglobin.[3b] The latter has another polarized band, at 1590 cm^{-1}, however, which, in light of the results in Table I, we reassign to the high-frequency A_{1g} skeletal porphyrin mode. The 1565 cm^{-1} mode can be attributed to the influence of the vinyl substituents. In ferrocytochrome c′,[9] a high-spin Fe(II) heme protein without vinyl substituents, the skeletal A_{1g} mode is found at 1583 cm^{-1}.

(9) T. C. Strekas and T. G. Spiro, *Biochim. Biophys. Acta*, **351**, 237 (1974).

(10) Ferrocytochrome c is used as a standard low-spin Fe(II) heme, rather than oxyhemoglobin, since the electronic effects of the bound oxygen ligand produce a Raman spectrum typical of low-spin Fe(III) instead of Fe(II).[3b]

(11) J. L. Hoard and W. R. Scheidt, *Proc. Nat. Acad. Sci. U.S.A.*, **70**, 3919 (1973).

(12) R. G. Little and J. A. Ibers, *J. Am. Chem. Soc.*, **96**, 4452 (1974).

(13) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

(14) The only marked discrepancy between observed and calculated patterns is that the B_{1g} mode at 1547 cm^{-1}, which appears not to change, is predicted to shift down by 20 cm^{-1}. In the calculation, this mode is strongly coupled to the B_{1g} mode at 1626 cm^{-1}, which does shift. A weakening of this coupling, which appears to be dictated by the observed shifts, could be effected by introducing an off-diagonal interaction constant. It is also conceivable that the observed band should be reassigned, e.g., to the B_{2g} mode calculated at 1476 cm^{-1}, which is insensitive to doming.

(15) T. Yamamoto, G. Palmer, D. Gill, I. T. Salmeen, and L. Rimai, *J. Biol. Chem.*, **248** 5211 (1973).

(16) L. A. Nafie, M. Pezolet, and W. L. Peticolas, *Chem. Phys. Lett.*, **20**, 563 (1973).

(17) H. Brunner, A. Mayer, and H. Sussner, *J. Mol. Biol.*, **70**, 153 (1972).

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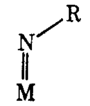
A New Reaction. Stereospecific Vicinal Oxyamination of Olefins by Alkyl Imido Osmium Compounds

Sir:

During our studies on the oxygen atom transfer chemistry of transition metal oxocompounds (**1**) with olefins, it occurred to us that similar reactions might take place with the nitrogen (**2**) and carbon (**3**) analogs of the oxo species. The

1



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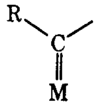

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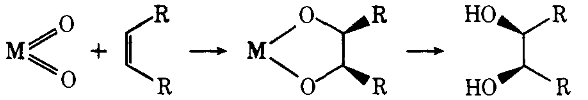
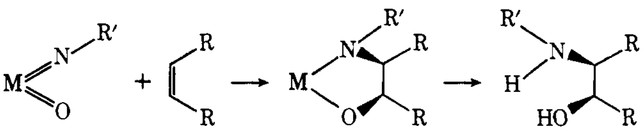
transition metal oxo compounds which react with olefins are typically d^0 substances having from two to four oxo groups. Cis dihydroxylation of olefins to form vicinal diols is a unique reaction of these oxidants (eq 1). We report here the first example of an aza analog of this transformation (eq 2).



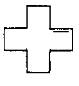
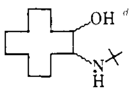
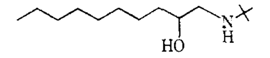
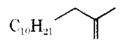
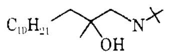
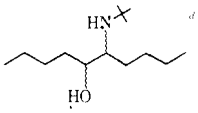
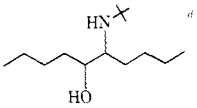
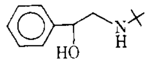
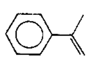
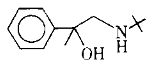
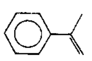
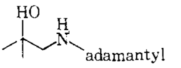
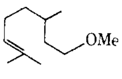
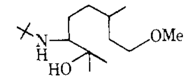
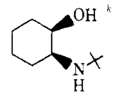
(1)



(2)

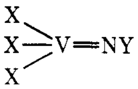
The only known d^0 alkyl imido transition metal species are compounds of vanadium[1] and osmium.[2] In the case of vanadium the compounds have the general structure **5**, and in the case of osmium only the single substance **6a** has been described.[2] In addition to the known *tert*-butyl imido compound **6a**, we have prepared the new adamantyl derivative **6b**. Both were synthesized in about 90% yield by treating the amine with OsO_4 in olefin-free pentane.[3] We were pleased to find that both imido reagents **6a** and **6b** react

Table I

Olefin	Amino alcohol[f]	% yield[a] amino alcohol	% yield[a] diol	Solvent
	 [d]	~3[b]	40[c]	CH_2Cl_2
1-Decene		62	6	CH_2Cl_2
		89	<1	Pyridine
		78[i]	<1	Pyridine
		82	<1	CH_2Cl_2
E-5-Decene	 [d]	20	50 (threo)	CH_2Cl_2
		>95	<3	Pyridine
Z-5-Decene	 [d]	0	53	CH_2Cl_2
		0	54 (erythro)[e]	CH_2Cl_2
		25	42	Pyridine
Styrene		37[h]	Trace	CH_2Cl_2
		52	<1	*t*-BuOH
		64	<1	THF
		92	<1	Pyridine
		74[e,g]		Pyridine
		93	<1	CH_2Cl_2
		62[e]		CH_2Cl_2
		0	78[e]	CH_2Cl_2
		38	45	Pyridine
Cyclohexene	 [k]	85[e]		Pyridine

[a] GLPC yield unless otherwise noted. All reactions were run with reagent 6a as described for styrene on a 0.3–0.4 mmol scale unless otherwise noted. [b] As amino acetate. [c] As diacetate. [d] Stereochemistry not determined. [e] Isolated yield. [f] All new compounds have been adequately characterized by spectral data and in most cases by analytical data. [g] MP 87–88°; lit.[8] 86–87°. [h] The low yield of product is believed to be caused by olefin polymerization and cleavage. [i] Bisulfite workup. [j] Oxidized with reagent 6b. [k] Cis geometry assigned because product was not identical with trans isomer prepared from cyclohexene oxide.

with a variety of olefins to afford, after reductive cleavage of the osmate esters, vicinal amino alcohols in fair to excellent yields (Table I).



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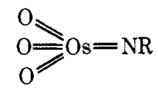


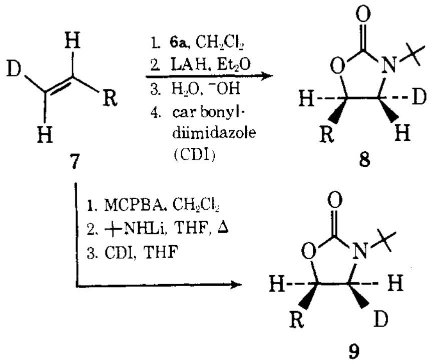
6a, R = *t*-Bu
b, R = 1-adamantyl

The stereochemistry of the addition was established to be cis by reaction of **6a** with the stereospecifically deuterated[4] 1-decene **7** which, after hydrolysis and derivitization, afforded the carbamate **8** (see Scheme I). The authentic diastereomer **9** was prepared as indicated from olefin 7; deuterium decoupled ^1H NMR spectra revealed that **8** contained less than 5% of its diastereomer **9.**

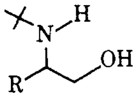
In all cases investigated to date, we have found that reagents **6** always form the new carbon–nitrogen bond at the least substituted carbon. The complete regiospecificity of the oxyamination of 1-decene was demonstrated by synthesizing the isomer **10**[5] (R = n-C_8H_{17}); **10** and **11** separate readily on GLPC and are distinguishable by TLC.

As revealed in Table I most of the reactions have been carried out in methylene chloride as solvent. More recently we have found that both the ratio of amino alcohol:diol and the rate of these reactions are increased by employing better coordinating solvents such as tetrahydrofuran and especially pyridine (see Table I). Thus this new reaction resembles that of OsO_4 with olefins for which pyridine is also the solvent of choice.

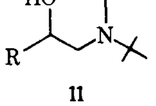
Scheme I



The following example describes a reaction carried out in pyridine; however, a similar procedure was used for reac-



10



11

Table II

Olefin	Relative rate[a]
Z-5-decene	1.0
Citronellol methyl ether	2.9
2-Methyl-1-tridecene	3.2
E-5-Decene	4.2
1-Undecene	8.1
Styrene	17

[a] Rates determined by competition[11] for reagent 6a in methylene chloride.

tions run in methylene chloride. To a solution of reagent **6a** (1.71 g, 5.54 mmol) dissolved in 50 ml of distilled pyridine (CaH_2) in a 500-ml round bottom at room temperature) was added 0.563 g (5.4 mmol) of styrene with stirring. The solution, initially burgundy red, became brownish black and opaque within 30 sec. Stirring was continued for 15 hr after which time the pyridine was removed[6] under high vacuum at room temperature. The black residue was dissolved in 250 ml of dry Et_2O and the flask was cooled in an ice bath and maintained under N_2. Excess LAH (2.44 g) was added slowly over a 5-min period with stirring. The brownish black mixture was allowed to warm to room temperature. Within 1 hr the heterogeneous mixture was tan colored. Stirring was continued for an additional hour. Dry ether, 100 ml, was added and the flask was cooled in an ice bath under N_2. The standard LAH workup of Mićović[7] was used. Rapid stirring was necessary and on occasion more ether was added to maintain stirring. The powdery precipitate was stirred for 1 hr before filtration. The filtrate was concentrated at reduced pressure yielding a brownish yellow oil. The product was bulb-to-bulb distilled (55°, 0.015 mm) affording a clear oil which upon crystallization from hexanes gave 0.772 mg (74%) of white crystals mp 87–88°C (lit.[8] 86–87°).

In Table II are given the relative rates for the reaction of the *tert*-butyl imido osmium reagent **6a** with several different olefins. The monosubstituted olefins react faster than the di- and trisubstituted olefins. As far as we know this is the only oxidant which has been reported[10] to exhibit this unusual selectivity. Even osmium tetroxide reacts faster with polysubstituted olefins than with monosubstituted olefins.[10]

One of the most remarkable aspects of this reaction is the preference exhibited by the trioxoalkyl imido reagents **6** for delivery of the nitrogen to one of the olefinic carbons. This reaction path would appear to be disfavored by the steric hindrance in the vicinity of the nitrogen produced by the tertiary alkyl substituents. This steric effect has prompted present efforts toward synthesis of analogs of **6** bearing smaller R groups. Such derivatives should allow formation of amino alcohols even with the more hindered olefins which presently give mainly diol with reagent **6a.** The vicinal oxyamination described here is the first instance of a nitrogen atom transfer which is directly related to the corresponding oxygen atom transfer process. Rather than being an isolated curiosity, we believe that it may be the first example of a new class of reactions wherein alkyl imido reagents (**2**), and perhaps also ylid reagents (**3**),[9] perform a variety of useful synthetic transformations analogous to those already known for oxoreagents (**1**).

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(3) The reagents **6** were prepared as follows. Equimolar amounts of amine and osmium tetroxide were dissolved in olefin-free pentane. After 5 min, the solvent was removed at reduced pressure taking care not to maintain the vacuum longer than necessary, as the resulting orange-red solid is volatile. Upon standing in the dark for 12 hr, the solid became yellow-brown. Sublimation of this residue afforded >90% yield of yellow imido osmium compounds **6** (**6a** mp 112 dec; **6b** mp 176–177°). This procedure is simpler and gives better yields than the literature (ref 2) procedure for the preparation of **6a.**

(4) G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 2753 (1967); U. G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **618**, 267 (1958).

(5) Compound **10** was prepared by lithium aluminum hydride reduction of the *tert*-butylimine derived from 1-acetoxy-2-decanone.

(6) If osmate ester cleavage under milder conditions is desired, the bisulfite reductive hydrolysis described by J. S. Baran (*J. Org. Chem.*, **25**, 257 (1960)) also gives good results. The pyridine need not be removed in such cases. We found the yields of amino alcohol somewhat lower using this procedure. In the case of 1-decene LAH reductive hydrolysis yielded 89% amino alcohol whereas cleavage with bisulfite yielded only 78%.

(7) V. M. Mićović and M. C. J. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

(8) J. A. DeYrup and C. L. Mayer, *J. Org. Chem.*, **34**, 175 (1969).

(9) The first d^0 transition metal ylid has just been reported: R. R. Schrock, *J. Am. Chem. Soc.*, **96**, 6796 (1974). It will be interesting to see if such species follow the same reactivity patterns which are emerging for the oxo and alkyl imido groups.

(10) We have also observed this same type of selectivity with $KMnO_4$ in acetic anhydride: K. B. Sharpless and D. R. Williams, submitted.

(11) Relative rates were determined by measuring the disappearance of olefins via GLPC. The following equation was used

$$k_{\mathrm{rel}} = \frac{k_A}{k_B} = \frac{\log\left(1 - \frac{(A)_c}{(A)_0}\right)}{\log\left(1 - \frac{(B)_c}{(B)_0}\right)}$$

$(A)_0$ and $(B)_0$ are the initial number of millimoles of olefins A and B, respectively. $(A)_c$ and $(B)_c$ are the number of millimoles consumed of the olefins.

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