References and Notes

(1) All E° values mentioned in this paper are formal potentials corresponding to the supporting electrolyte concentration employed, 0.1 M tetrabutylammonium perchlorate.
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Stereospecific Vicinal Oxyamination of Olefins by Alkylimidoosmium Compounds

Donald W. Patrick, Larry K. Truesdale, Scott A. Biller, and K. Barry Sharpless*

Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

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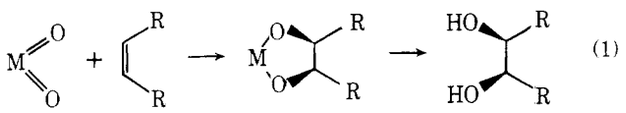
The reaction of trioxo(*tert*-alkylimido)osmium(VIII) complexes with a variety of olefins (30 different cases) affords, after reduction of the intermediate osmate esters, vicinal amino alcohols in fair to excellent yields. The synthetic utility of this new reaction was evaluated by examining the effects of solvent, temperature, olefin substitution patterns, and functional groups. Where possible the imidoosmium(VIII) reagents were compared to osmium tetroxide. Stereospecific preparations of both (*E*)-1-deuterio-1-decene and (*Z*)-1-deuterio-1-decene are described.

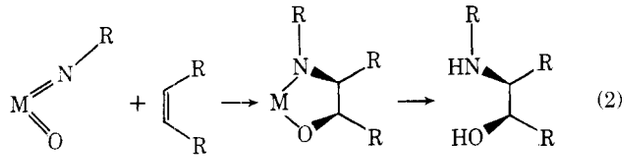
During our studies on oxygen atom transfer chemistry of transition metal oxo compounds (**1**) with olefins, it occurred to us that similar reactions might take place with the nitrogen (**2**) and carbon (**3**) analogues of the oxo species. The transition

1 **2** **3**

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 further examples of an aza analogue of this transformation (eq 2).[1]

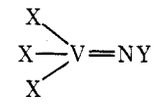


(1)



(2)

The only known d^0 alkylimido transition metal species are compounds of vanadium[2] and osmium.[3] In the case of vanadium the compounds have the general structure **5**, and in the case of osmium only two substances (**6a**[3a,b] and the related monoimido species derived from *tert*-octylamine[3b]) have been described. In addition to the known *tert*-butylimido compound **6a**, we have prepared the new adamantyl derivative **6b** and the *tert*-amyl derivative **6c**. All three were synthesized in about 90% yield by treating the amine with OsO_4 in olefin-free pentane or CH_2Cl_2. We were pleased to find that the imido reagents all reacted with a variety of olefins to afford, after reductive cleavage of the osmate esters, vicinal tertiary alkylamino alcohols in fair to excellent yields. The mode of addition of reagents **6** has been shown to be stereospecific and in most cases highly regioselective.



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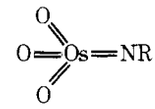

6a, R = *tert*-butyl
b, R = 1-adamantyl
c, R = *tert*-amyl

A number of methods are available for synthesis of β-amino alcohols.[4] Each method varies with respect to starting material, overall yield, regiospecificity, and stereochemistry, However, only this new procedure allows direct cis addition of the oxygen and nitrogen moieties to the olefinic bond.

Results and Discussion

Stereochemistry. The mode of the addition of alkylimidoosmium compounds to olefins in CH_2Cl_2 was established

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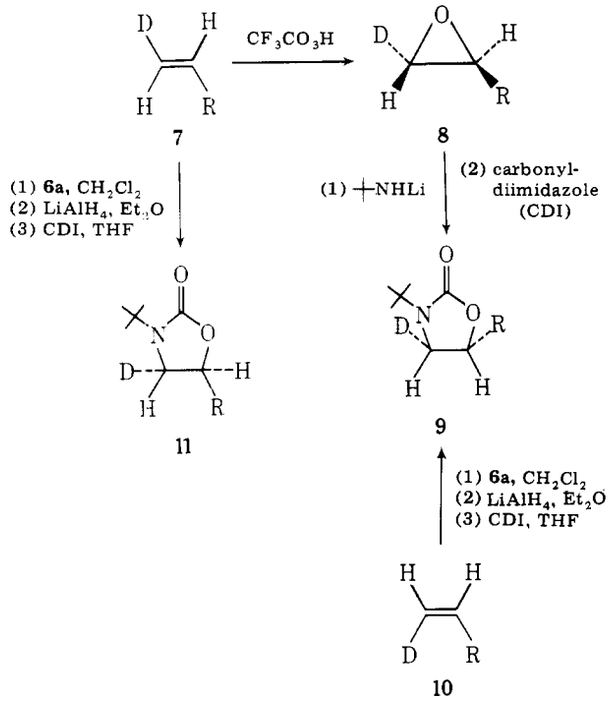
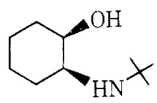
Scheme I

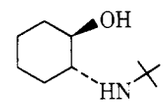


to be cis by reaction of **6a** with the stereospecifically deuterated 1-decenes **7** and **10**, which after hydrolysis and derivitization afforded carbamates **11** and **9**, respectively. The authentic diastereomer **9** was prepared as indicated from olefin **7**; deuterium-decoupled ^1H NMR spectra revealed that **11** contained less than 5% of its diastereomer **9**. Similarly, oxyamination of **10** afforded **9**, which contained less than 5% of its diastereomer **11** (Scheme I).

The stereochemistry of the addition in pyridine was established to be cis by reaction of **6a** with cyclohexene to afford, after hydrolysis of the osmate ester, the amino alcohol **12**. The diastereomer **13**, prepared by opening cyclohexene oxide with



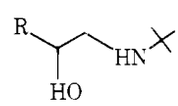
12



13

tert-butylamine, was shown to be different from **12** by GLC, NMR and IR spectroscopy, and melting point. Oxyamination of (*E*)- and (*Z*)-1-phenylpropene with **6a** provided further evidence for a stereospecific addition in pyridine since the two amino alcohol regioisomers obtained from the *E* olefin were nonidentical by GLC and ^1H NMR spectroscopy with the two regioisomers obtained from the *Z* olefin.

Regioselectivity and Solvent Effects. 1-Decene reacts with **6a** in CH_2Cl_2 to afford, after reductive cleavage, a 62% yield of amino alcohol **14** (R = n-C_8H_{17}) and 6% of the 1,2-diol.



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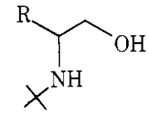


15

The *complete* regiospecificity of the oxyamination was demonstrated by synthesis of the isomer **15** (R = n-C_8H_{17}); **14** and **15** separate readily on GLC and are distinguishable by TLC. In all cases investigated to date, we have found that reagents **6** always form the new carbon–nitrogen bond at the least substituted carbon.

Solvent plays an important role in the oxyamination process. A poor yield of 2-(*tert*-butylamino)-1-phenylethanol was obtained when **6a** was allowed to react in CH_2Cl_2 with styrene. Benzyl alcohol was another product, presumably produced by oxidative cleavage of the intermediate osmate ester (due to the reductive nature of the workup ($LiAlH_4$), we observed benzyl alcohol rather than benzaldehyde). Henbest[5] found that the reaction of stilbene with OsO_4 in noncoordinating solvents such as cyclopentane afforded considerable benzaldehyde; addition of several equivalents of pyridine completely suppressed the production of benzaldehyde. We have also found that significantly higher yields of amino alcohol were obtained as the coordinating ability of the solvent increased. Yields of amino alcohol from the reaction of styrene with **6a** in CH_2Cl_2, *tert*-butyl alcohol, THF, *tert*-butylamine, and pyridine are shown in Table I. The highest yield of amino alcohol was obtained with pyridine as solvent. *In all of the cases studied where a particular olefin was oxyaminated in CH_2Cl_2 and in pyridine, reactions carried out in pyridine gave consistently higher yields of amino alcohol and less diol.* We have also found that pyridine enhances the rate of addition of the imido compounds to olefins; this parallels a similar observation by Criegee et al.[6] regarding the addition of OsO_4 to olefins.

The reaction of (*E*)-5-decene with **6a** in CH_2Cl_2 afforded only a 20% yield of the amino alcohol and a 50% yield of diol. When oxyaminated in pyridine, the same substrate gave greater than 95% amino alcohol and less than 3% diol. Even more striking are the results from the oxyamination of (*Z*)-5-decene. Only the erythro diol was obtained when the reaction was run in CH_2Cl_2. No amino alcohol was observed by GLC. In pyridine at room temperature the major product was still diol (42%), but 25% amino alcohol was also observed. However, when the reaction of (*Z*)-5-decene was conducted in pyridine at 0 °C (6 days), a 65% yield of amino alcohol and only a 25% yield of diol were observed, demonstrating that the amino alcohol to diol ratio is also temperature sensitive. Despite the cis nature of the double bond in norbornene, cyclohexene, and (*Z*)-1-phenyl-1-propene, good to excellent yields of amino alcohol were achieved at room temperature in pyridine.

In the case of 1-phenyl-2-alkyl-disubstituted double bonds, carbon–nitrogen bond formation usually occurred with some preference for the olefinic carbon adjacent to the aromatic system. Reactions of (*Z*)-1-phenyl-1-propene, (*E*)-1-phenyl-1-propene, and 1,2-dihydronaphthalene with **6a** all afforded mixtures of the 1- and 2-amino alcohol regioisomers in which benzylic amination predominated.

The reaction of trisubstituted olefins with **6** afforded β-amino alcohols in fair to good yield. Citronellol methyl ether gave primarily diol when the reaction was carried out in CH_2Cl_2 and diol and amino alcohol in nearly a 1:1 ratio when the reaction was carried out in pyridine. However, 1-phenylcyclohexene, 1-methylcyclopentene, and 1-phenyl-2-methylpropene all gave the β-amino alcohol as the major product (see Table I). The tetrasubstituted double bond of tetramethylethylene afforded only diol in 82% yield when reacted with **6a** in pyridine; no β-amino alcohol could be detected by NMR spectroscopy.

Dependence of Rate on Olefin Substitution. Table II presents the relative rate data for the consumption of olefins in the reaction of **6a** in CH_2Cl_2 with a series of mono-, di-, and trisubstituted olefins. Interestingly, the di- and trisubstituted olefins reacted slower with the imido reagent than the monosubstituted olefins. (The relative rate data for the oxidation of olefins with OsO_4, unlike the imido reagent, demonstrate that OsO_4 reacts faster with the more highly substituted olefins.[7]) The only other known olefin oxidations which show this rare type of selectivity are $KMnO_4$ in acetic anhydride[7] and aminopalladation.[8] For a given type of substitution pattern, reaction with the imido compound occurs faster when the

Table I

Olefin	Registry no.	Amino alcohol[a]	Registry no.	Yield of amino alcohol,[b] %	Yield of diol, %	Solvent
(*E*)-Cyclododecene	1486-75-5	2-(*tert*-Butylamino)cyclododecanol[c]		3[d]	40[e]	CH_2Cl_2
1-Decene	872-05-9	n-C_8H_{17}(OH)CHCH$_2$NH(*t*-Bu)	55915-71-4	63	6[f]	CH_2Cl_2
				89	<1	Pyridine
				78[g]	<1	Pyridine
Styrene	100-42-5	PhCH(OH)CH$_2$NH(*t*-Bu)	18366-40-0	37[h]	Trace	CH_2Cl_2
				52	<1	*t*-BuOH
				64	<1	THF
				77	<1	*tert*-Butylamine
				92	<1	Pyridine
				74[i,j]		Pyridine
2-Methyl-1-tridecene	18094-01-4	n-$C_{11}H_{23}$(Me)C(OH)CH$_2$NH(*t*-Bu)	55915-72-5	82	<1[k]	CH_2Cl_2
α-Methylstyrene	98-83-9	Ph(Me)C(OH)CH$_2$NH(*t*-Bu)	55915-75-8	93	<1[l]	CH_2Cl_2
α-Methylstyrene		Ph(Me)C(OH)CH$_2$NH(1-admantyl)[m]	55912-76-9	62	<1	CH_2Cl_2
(*E*)-5-Decene	7433-56-9	*threo*-6-(*tert*-Butylamino)-5-decanol[c]	55915-73-6	20	50 (threo)	CH_2Cl_2
				>95	<3	Pyridine
(*Z*)-5-Decene	7433-78-5	*erythro*-6-(*tert*-Butylamino)-5-decanol[c]	55912-74-7	0	53	CH_2Cl_2
				0	54 (erythro)[i]	CH_2Cl_2
				25	42	Pyridine
				65	25	Pyridine (0 °C)
Cyclohexene	110-83-8	*cis*-2-(*tert*-Butylamino)cyclohexanol	55915-78-1	85[i]		Pyridine
Cyclohexene		*cis*-2-(1-Adamantylamino)cyclohexanol[c,m]	65760-97-6	79[i]		Pyridine
Norbornene	498-66-8	*cis-exo*-3-(*tert*-Butylamino)bicyclo[2.2.1]-heptan-2-ol	65760-98-7	94[i]		Pyridine
1,2-Dihydronaphthalene	447-53-0	*cis*-2-(*tert*-Butylamino)-1-hydroxytetralin (69)[o,c]	65760-99-8	38[i,n]	*q*	Pyridine
		cis-1-(*tert*-Butylamino)-2-hydroxytetralin (31)[o,c]	65761-00-4			
p-Cyano-α-methylstyrene	19956-03-7	(*p*-Cyanophenyl)(Me)C(OH)CH$_2$NH(*t*-Bu)	65761-01-5	40[i,g,p]		Pyridine
p-Chloro-α-methylstyrene	1712-70-5	(*p*-Chlorophenyl)(Me)C(OH)CH$_2$NH(*t*-Bu)	65761-02-6	97[i]		Pyridine
p-Methyl-α-methylstyrene	1195-32-0	(*p*-Methylphenyl)(Me)C(OH)CH$_2$NH(*t*-Bu)	65761-03-7	95[i]		Pyridine
p-Methoxy-α-methylstyrene	1712-60-2	(*p*-Methoxyphenyl)(Me)C(OH)CH$_2$NH(*t*-Bu)	65761-04-8	70[i]		Pyridine
p-*N*,*N*-Dimethylamino-α-methylstyrene	25108-56-9	(*p*-*N*,*N*-Dimethylaminophenyl)(Me)C(OH)-CH$_2$NH(*t*-Bu)	65761-05-9	88[i]	10[i]	Pyridine
(*Z*)-1-Phenylpropene	766-90-5	*erythro*-PhCH[NH(*t*-Bu)]CH-(OH)Me (97)[r,c]	65761-06-0	92[i]		Pyridine
		erythro-PhCH(OH)CH[NH(*t*-Bu)]Me (3)[r,c]	65761-07-1			
(*E*)-1-Phenylpropene	873-66-5	*threo*-PhCH[NH(*t*-Bu)]CH(OH)Me (76)[s,c]	65761-08-2	91[i]		Pyridine
		threo-PhCH(OH)CH[NH(*t*-Bu)]Me (24)[s,c]	65760-82-9			
Citronellol methyl ether	55915-70-3	MeO(CH$_2$)$_2$CH(Me)CH$_2$CH$_2$CH[NH(*t*-Bu)]-C(OH)Me$_2$	55915-77-0	0	78[i]	CH_2Cl_2
				38	45	Pyridine
1-Phenyl-2-methylpropene	768-49-0	PhCH[NH(*t*-Bu)]C(OH)Me$_2$	65760-83-0	88[i]	0[t]	Pyridine
1-Phenylcyclohexene	771-98-2	2-(*tert*-Butylamino)-1-phenylcyclohexanol[c]	65760-84-1	65[i]	8	Pyridine
1-Methylcyclopentene	693-89-0	2-(*tert*-Butylamino)-1-methylcyclopentanol[c]	65760-85-2	66[i]		Pyridine
Tetramethylethylene	563-79-1				81[i]	Pyridine

[a] All new compounds have been characterized by spectral and analytical data. [b] GLC yield unless otherwise noted. [c] The stereochemistry was not proven in these cases. However, we feel that there is little doubt that they are the products resulting from stereospecific cis addition of the amino and hydroxyl moieties to the olefin. [d] As amino acetate. [e] As diacetate. [f] A known diol (ref 22). [g] Bisulfite workup. [h] The low yield of product is believed to be caused by oxidative cleavage of the osmate ester intermediate. [i] Isolated yield. [j] Mp 87–88 °C (lit.[21] mp 86–87 °C). [k] A known diol (ref 9). [l] A known diol (ref 23). [m] Oxidized with reagent **6b**. [n] The low yield is believed to be caused by ~25% impurity in the starting material. [o] The numbers in parentheses refer to the ratio of regioisomers. [p] The low yield is believed to be due to the bisulfite workup and impurities in the starting olefin. [q] A known diol (ref 27). [r] Assumed to be the erythro regioisomers (see *c* above). [s] Assumed to be the threo regioisomers (see *c* above); all four of the amino alcohol isomers derived from the 1-phenylpropenes are separable by GLC. [t] A known diol (ref 26).

olefin is conjugated to an aromatic ring, e.g., styrene vs. 1-decene and 2-methyl-1-tridecene vs. α-methylstyrene.

Inductive electron-withdrawing groups in the vicinity of an olefin have little effect upon the rate of oxidation as evidenced by the fact that phenyl allyl ether reacted 0.95 times as fast as 4-phenyl-1-butene in pyridine. In contrast, the geometry of the olefin is important. Reagent **6a** reacts 4.2 times faster in methylene chloride with (*E*)-5-decene than with (*Z*)-5-decene; however, the product analysis shows that (*Z*)-5-decene gives exclusively diol while (*E*)-5-decene gives both amino alcohol and diol. The oxyamination of (*Z*)- and (*E*)-1-phenylpropene in pyridine affords only β-amino alcohols and no diol. A competition experiment between these two olefins in pyridine showed that the *E* isomer reacted 4.9 times faster than the *Z* isomer.

Since it has been shown[7,9] for OsO_4 that as the coordinating ability of the solvent is increased the rate differences for olefin oxidation are compressed (not reordered), it is reasonable to anticipate an even larger rate difference for the oxyamination of the 1-phenylpropenes in CH_2Cl_2. However, as the rates become slower, diol formation also begins. From a synthetic standpoint the differences in rate demonstrated by the imido compound are not in general great enough to anticipate selective oxidation of polyenes.

Functional Group Compatibility. The synthetic utility of a reagent is dependent on the selectivity it demonstrates for reaction with a specific functional group. The results of the oxyamination of a series of monosubstituted olefins containing functional groups sensitive to oxidation are shown in Table III. Only 1-phenylbut-3-en-1-ol and *N*-allylaniline afforded,

Table II. Relative Rate Data for Oxidation of Olefins with 6a in CH_2Cl_2

Olefin	Relative rate[a]
(*Z*)-5-Decene	1.0
Citronellol methyl ether	2.9
2,3-Dimethyl-2-octene	3.2
2-Methyl-1-tridecene	3.2
(*E*)-5-Decene	4.2
α-Methylstyrene	6.2
1-Undecene	8.1
Styrene	17.0

[a] Based on the disappearance of olefin.

in addition to the desired amino alcohol, other uncharacterized products. The results of the oxidation of a series of para-substituted α-methylstyrenes by **6a** are displayed in Table I. In general, we have found that imido reagents **6** are milder oxidants than OsO_4. This fact is well illustrated by the oxidation of *N*-allylaniline with OsO_4 which gave only a 10% yield of diol and numerous other products,[10] whereas reagent **6a** gave a 50% yield of amino alcohol. Although we have not screened an extensive series of oxidatively sensitive compounds, we feel that any functional group that is compatible with OsO_4 will be compatible with the imido compounds.

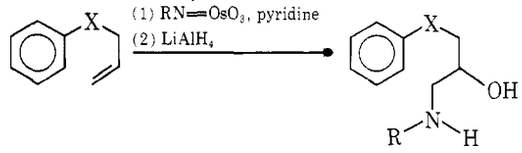
Attempts at Forming Imido Compounds with Other Amines. The usefulness of the oxyamination is limited by the fact that only a select number of primary amines bound to a tertiary carbon center form stable crystalline imido compounds. Attempts to form stable trioxo(alkylimido)osmium(VIII) compounds by methods similar to that used to prepare reagents **6** with the following amines failed: ethyl 2-amino-2-methylpropionate, 2-amino-2-cyanopropane, 1-phenyl-2-amino-2-methylpropane, 1-chloro-3-amino-3-methylbutane, 1-hydroxy-2-amino-2-methylpropane, tritylamine, 1,4-diamino-1,1,4,4-tetramethylbutane, methoxyamine, *p*-toluenesulfonamide, triphenylsilylamine, 1-amino-1-phenylcyclohexane, cyanamide, aniline tosylhydrazine, and 1-amino-1,2,2,3-tetramethylcyclopentane.

In many cases the amine complexed with the OsO_4 to form an unstable red-orange crystalline intermediate which decomposed, occasionally violently, upon warming. Similar complexes were observed during the preparation of reagents **6**, but these intermediates afforded only diols upon reaction with olefins. Thus, the addition of 1 equiv of 1-decene to a solution containing 1 equiv of OsO_4 and 1 equiv of *tert*-butylamine in pentane afforded 1,2-decanediol as the sole product after $LiAlH_4$ workup. The only method we have found to successfully convert the intermediate to the imido compounds **6** was to store it in the dark at room temperature free of solvent in the solid state for 6–12 h. Unfortunately only three of the tertiary amines that were tested survived the solid-state reaction.

The orange solutions of the osmium tetroxide–amine complexes are very stable in the usual organic solvents, revealing no tendency for dehydration to give imido species **6**. More recently,[36] however, we have found that imido complexes **6a** and **6c** are very readily formed by reaction of OsO_4 with the corresponding amines in water (ref 36 contains the experimental details for these preparations). The aqueous procedure fails for amines (e.g., adamantylamine) which are not soluble in water. Even in such cases it should be possible to avoid the sublimation of the imido reagent (e.g., **6b**) by allowing the solid amine–OsO_4 complex to stand overnight (solid-state dehydration step) and then using this crude reagent directly by simply dissolving it in pyridine and adding the olefin substrate.

Reactions of the Imido Reagents with 4-(*tert*-Butyl)-methylenecyclohexane. Henbest[11] used 4-(*tert*-butyl)-methylenecyclohexane as a stereochemical probe for epoxidation by perlauric acid to determine the preference of the reagent for axial vs. equatorial attack. An analogous study with imido compounds **6** was undertaken (Table IV). In both methylene chloride and pyridine imido reagents **6** all showed substantial preference for the sterically less hindered equatorial mode of attack. The preference for equatorial attack is not surprising considering the substantial bulk of these imidoosmium compounds (the oxo bond lengths in OsO_4 are 1.74 Å[12]); notice also that the variation of the alkyl group bound to nitrogen does not effect the ratio of axial to equatorial attack. What is surprising is that a similar selectivity was observed with OsO_4 itself. In fact, OsO_4 even showed a slightly greater preference for equatorial attack than the imido species. An explanation of these apparent anomalies must await better understanding of the mechanisms of these reactions.

Table III[a,d]



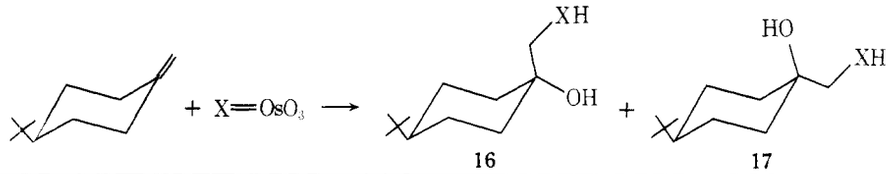
R	X, % CHOH	O	S	NH
tert-Butyl	50[b]	70[c]	66[b]	55[c]
1-Adamantyl		66[c]		
tert-Amyl		88[b]		

[a] Isolated yields. [b] Chromatographed on Florisil. [c] Chromatographed on silica gel. [d] Consistently higher yields have been obtained when chromatographic isolation was accomplished with Florisil instead of silica gel.

Behrman et al.[13] and Criegee et al.[6] have reported the isolation of the OsO_4 pyridine complex. Osmium tetroxide has a very strong oxo stretch (CCl_4) at 960 cm^{-1}. We found that addition of 1 equiv of pyridine showed a new, very strong absorption band at 925 cm^{-1}. Additional equivalents of pyridine diminished the intensity of the 960-cm^{-1} band further with concommitant increase in the intensity of the 925-cm^{-1} band. Yet, even after 3 equiv of pyridine was added the 960-cm^{-1} band did not disappear completely. Imido compound **6a** has two strong oxo stretches (CCl_4) at 925 and 912 cm^{-1}. Addition of 4 equiv of pyridine did not effect the intensity of the oxo bands or produce any new bands in the IR spectrum attributable to oxo stretches. The imido compound is clearly reluctant to add pyridine to its coordination sphere. Pyridine obviously plays an important role during the oxyamination of olefins with imido reagents because of the dramatic changes in diol to amino alcohol ratios observed when it is present. It is, however, unclear at what point along the reaction pathway pyridine coordinates with the metal center.

Optimum Conditions for Osmate Ester Cleavage. During our initial investigations on the oxidation of olefins with **6**, problems were encountered with the cleavage of the intermediate osmate esters. We found that the majority of methods in the literature were only moderately satisfactory. A study was undertaken to determine the best method for ester cleavage. In five separate reactions the osmate ester obtained by reacting 1-decene with **6a** was cleaved by one of the methods shown in Table V. Of the methods tested, only the $LiAlH_4$ and bisulfite cases afforded good yields of the amino alcohol. We have found that $LiAlH_4$ is the best cleavage reagent for osmate esters of oxyaminated olefins which contain no $LiAlH_4$-labile functional groups. In cases where $LiAlH_4$ could not be used the bisulfite workup has proven satisfactory. More recently in a related system we have found that bisulfite reductions of osmate esters are improved by heating to 60–80

Table IV



X	Solvent	16, %	Registry no.	17, %	Registry no.	Yield (16 + 17), %
+N(6a)	Pyridine	81	65760-86-3	19	65760-87-4	93
+N(6a)	CH_2Cl_2	85		15		
+N(6c)	Pyridine	81	65760-88-5	19	65760-89-6	81
(1-Adamantyl)-N (**6b**)	Pyridine	81	65760-90-9	19	65760-91-0	91
O	Pyridine	86	60380-83-8	14	60380-79-2	
O	CH_2Cl_2	82		18		

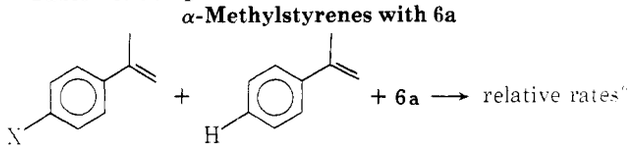
Table V. Osmate Ester Cleavage

1-decene + O_3Os = N + → osmate ester → amino alcohol

Reaction solvent	Ester cleavage solvent	Cleavage reagents	Yield of amino alcohol,[a] %
Pyridine	Et_2O	$LiAlH_4$[b]	89
Pyridine	Pyridine	Bisulfite[c]	78
Dioxane[d]	Dioxane	H_2S[e]	20
THF[f]	THF	H_2S	21
Pyridine	H_2O	HCl, H_2S[g]	No amino alcohol
Pyridine	CH_2Cl_2/H_2O	KOH, mannitol[h]	Bad emulsion

[a] Determined by GLC. [b] Reference 14. [c] Reference 15. [d] Pyridine (10 equiv) was added. [e] Reference 16. [f] Pyridine (5 equiv) was added. [g] Reference 17. [h] Reference 6.

Table VI. Competitive Oxidations of Para-Substituted α-Methylstyrenes with 6a



X	$\frac{k_X}{k_H}$ (CH_2Cl_2)	$\frac{k_X}{k_H}$ (pyridine)
$N(Me)_2$	4.26	1.63
OMe	1.49	1.04
Me	1.14	1.01
H	1.00	1.00
Cl	0.95	1.23
CN	1.93	1.53

[a] Based on disappearance of olefin.

°C for several hours.[24] We would also recommend heating in these bisulfite workups as a likely means of increasing the yields of amino alcohols.

Electronic Effects. Hammett Study. In order to become better acquainted with the electronic factors associated with the reactions of imidoosmium compounds with olefins, a Hammett study was undertaken. Relative rates for the addition of **6a** to a series of para-substituted α-methylstyrenes in pyridine and methylene chloride were determined via competition studies (see Table VI). Authentic β-(*tert*-butylamino) alcohols were prepared and characterized in separate experiments by the addition of **6a** to the appropriate α-methylstyrene (see Table I).[18] A plot of the data shown in Table VI gave U-shaped curves for reactions conducted in both methylene chloride and pyridine. Dondoni observed a similar phenomenon for the 1,3-dipolar addition of nitrile oxides to para-substituted styrenes.[31] Firestone[19,20] rationalized the U-shaped Hammett plot obtained by Dondoni by suggesting that the 1,3-dipolar addition proceeded with diradical character in the transition state, and as such, X groups conjugated to an unsaturated radical center will stabilize the radical intermediate relative to X = H. It is interesting to note that Henbest has found that the addition of OsO_4 to a series of para- and meta-substituted stilbenes gave a normal Hammett plot with $\rho = -0.55$.[5]

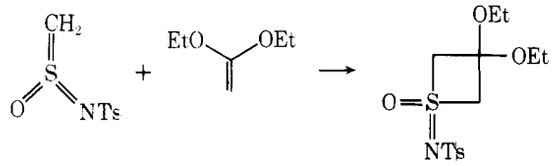
Conclusions

We wish to point out a number of features which make this new synthetic method of considerable interest. (a) The stereochemistry of the addition was shown to be exclusively cis. (b) The reaction of monosubstituted olefins with **6** gave good to excellent yields of the amino alcohol, and the new nitrogen–carbon bond formed exclusively at the terminal olefinic carbon. (c) The reaction of trans disubstituted olefins with **6** at room temperature in pyridine gave excellent yields of amino alcohol, but the ratio of regioisomers was dependent upon the substrate. (d) The yields of amino alcohol from the reaction of **6** with cis disubstituted olefins in pyridine were strongly dependent upon the substrate. The ratio of β-amino alcohol to diol from (*Z*)-5-decene exhibited a marked dependence upon solvent and temperature. (e) The reaction of geminal disubstituted olefins with **6** gave good to excellent yields of β-amino alcohols in pyridine or CH_2Cl_2, and the new carbon–nitrogen bond formed exclusively at the least substituted olefinic carbon. (f) The reaction of trisubstituted double bonds with **6** in pyridine gave moderate to excellent yields of amino alcohol depending on the substrate; the new carbon–nitrogen bond formed exclusively at the least substituted olefinic carbon. (g) The only tetrasubstituted olefin tested, tetramethylethylene, gave only diol upon reaction with **6a** in pyridine at room temperature. (h) Pyridine was the best solvent for the

oxyamination of olefins with reagents **6**. (i) $LiAlH_4$ was the best reagent for cleavage of the intermediate osmate esters. (j) The imido reagents **6** were milder oxidants than OsO_4.

This new synthetic transformation suffers from two important limitations. It requires a stoichiometric amount of osmium reagent **6**, and it is difficult to remove the *tert*-alkyl group from the products. However, a new catalytic procedure for oxyamination of olefins solves both of these problems.[24,37] More recently, it has been found that polyimidoosmium complexes effect cis diamination of olefins.[36]

Although in the present work some data were collected which are also relevant to the mechanism of reaction of these imidoosmium reagents **6** with olefins, we prefer to postpone mechanistic considerations for a later publication. That publication will deal with the general problem of the mechanisms of reactions of olefins with oxo (M=O), imido (M=NR), and ylide ($M=CR_2$) species of both transition metal and main group elements.[25] However, it is worth pointing out at this time that it is remarkable that the trioxoalkylimido reagents **6** exhibit such a strong preference for delivery of the nitrogen to one of the olefinic carbons. This reaction path would appear to be disfavored by the steric bulk in the vicinity of the nitrogen produced by the tertiary alkyl substituents. One finds precedent for this preference of nitrogen over oxygen in the reactions of related sulfur species with olefins. The most elegant example is that of Johnson in



which the iminosulfene reacts with an enol ether to give the [2 + 2] adduct.[29] In this instance the olefin has a smorgasbord of the first row atoms (C, N, and O) to choose from, and it selects carbon, the element furthest to the left. This rule of selection (C > N > O) appears to hold for all known [2 + 2] and [2 + 4] additions of other similar sulfur compounds with olefins and dienes. Whatever the origin of this important effect, it seems that it may have validity for elements other than sulfur.

Experimental Section

Analytical GLC was done on one of the following columns: A, glass, 6 ft × 2 mm, 10% UCW-98 on 80–100 Gas Chrom Q; B, glass, 6 ft × 2 mm, 3% OV-17 on 80–100 Gas Chrom Q; C, glass, 6 ft × 2 mm, 3% FFAP on 80–100 Gas Chrom Q. Preparative GLC was done on one of the following columns: D, copper, 6 ft × 0.25 in, 10% UCW-98 on 80–100 Gas Chrom Q; E, copper, 8 ft × 0.25 in, 20% SE-30 on 45–65 Chromosorb W. All GLC yields were determined by using hydrocarbon internal standards.

Starting Materials. Methylene chloride was purified by stirring it over portions of concentrated sulfuric acid until the acid layer remained colorless. The methylene chloride layer was washed with 10% sodium bicarbonate, water, and brine and dried ($MgSO_4$). Distillation from calcium hydride afforded dry, olefin-free methylene chloride. Pentanes were stirred over portions of concentrated sulfuric acid until the acid layer remained clear. The pentanes were further purified by stirring them over 10% aqueous potassium permanganate overnight. The pentane layer was washed with water and brine and dried ($MgSO_4$). Distillation from sodium metal afforded dry, olefin-free pentanes. Reagent grade pyridine was distilled from calcium hydride and stored over 4A molecular sieves. Ethyl ether was distilled from lithium aluminum hydride before use. Tetrahydrofuran was distilled from sodium–benzophenone, and dioxane was distilled from sodium metal.

Note on Abbreviated Format: Due to the large number of olefins reacted and to the similar nature of the initial stages of each oxyamination, only purification and spectral details are generally given for each case. Thus, the experimental details usually begin following the workup (either $LiAlH_4$ or bisulfite as indicated in parentheses). The general procedures for starting the oxyamination reactions and the $LiAlH_4$ and bisulfite workups are described below.

Oxyamination of Olefins. General Procedure. To an ca. 0.1 M solution of 1 equiv of the trioxo(alkylimido)osmium(VIII) species in olefin-free methylene chloride or pyridine was added 1.0 equiv of olefin with stirring. The reaction mixture darkened at various rates depending on the olefin. The reaction was kept in the dark for 12 h to 2 days depending on the olefin. The resulting osmate ester was cleaved by one of the following methods.

A. Bisulfite Workup. The procedure of Baran[15] was followed. If the initial reaction was conducted in methylene chloride, it was removed at reduced pressure. The brown residue was then subjected to a solution of the following description: for each millimole of osmate ester, 10 mL of pyridine and a solution of 0.5 g of sodium bisulfite in 8 mL of water were added. If the initial reaction solvent was pyridine, one only added the sodium bisulfite solution (0.5 g in 8 mL of H_2O/mmol of osmium reagent). The reaction mixture was stirred for at least 12 h at room temperature (more recent results[24] indicate that heating at 60–80 °C for several hours might be superior, especially in difficult cases) and then extracted once with 40 mL of chloroform (per mmol of osmate ester) and twice with 12 mL of chloroform. The combined chloroform layers were evaporated to dryness at reduced pressure. Further purification was accomplished by standard methods.

B. Lithium Aluminum Hydride Workup. If the reaction was conducted on a 5-mmol scale, we found that a 200-mL flask was the best size for the oxyamination. Due to the heterogeneous nature of the reductive cleavage, considerable volumes of anhydrous ether were necessary to maintain stirring.

Whether the initial solvent was methylene chloride or pyridine, solvent removal at reduced pressure was necessary. Pyridine was removed under high vacuum while methylene chloride was easily removed at aspirator pressure. The brownish-black osmate ester was "dissolved" in anhydrous ether. Generally, 25 mL/mmol of osmate ester was optimum. The reaction vessel was cooled in an ice bath and maintained under nitrogen. To the stirred reaction vessel was added 10 equiv of $LiAlH_4$ (relative to starting osmium reagent). The reaction mixture was stirred for 12 h at room temperature before quenching according to the procedure of Mićović and Mihailovic,[30] a description of which follows. The reaction mixture was cooled in an ice bath and maintained under nitrogen. For every x g of $LiAlH_4$ used in the reductive cleavage, x mL of water was cautiously and slowly added to the reaction mixture. (Rapid stirring was maintained throughout the quench, and more anhydrous ether was added when necessary.) After the addition of water, x mL of 15% aqueous sodium hydroxide was added slowly, followed by $3x$ mL of water. Best results were obtained when the hydrolyzed mixture was stirred for at least 12 h. After 12 h the mixture was filtered and the pad of osmium and aluminum salts was washed once with anhydrous ether. The ether filtrate was concentrated at reduced pressure. Further purification was effected by standard techniques.

Trioxo(*tert*-butylimido)osmium(VIII) (6a). To a 200-mL recovery flask was added 10.0 g (39.4 mmol) of osmium tetroxide and 50 mL of olefin-free pentane. After 5 min of stirring most of the tetroxide had dissolved, and 4.2 g (39.5 mmol) of *tert*-butylamine was added. A rapid exothermic reaction followed causing boiling of the pentane, and a large mass of red-orange crystals settled to the bottom of the flask. The reaction was stirred for 30 min before the solvent was removed at reduced pressure. Care must be taken not to maintain the vacuum longer than necessary because the solid is volatile. The contents of the flask were stored in the dark overnight (16 h) at room temperature before being sublimed (55 °C, 0.005 mm) to afford 11.10 g (91%) of a yellow solid, mp 112 °C dec (see ref 36 for a more convenient preparation of **6a** and **6c**).

Trioxo(1-adamantylimido)osmium(VIII) (6b). To a 200-mL recovery flask was added 6.0 g (23.6 mmol) of osmium tetroxide and 15 mL of olefin-free methylene chloride. To the resulting osmium solution was added 3.57 g (23.6 mmol) of 1-adamantylamine in 75 mL of methylene chloride. A golden-yellow solution resulted, and the addition of 30 mL of pentane did not force precipitation of a solid. The solvent was removed at reduced pressure, leaving behind a red-orange solid. After 6 h of storage in the dark, the residue was a dark yellow-brown color. Sublimation (0.005 mm, 130–135 °C) afforded 8.32 g (91%) of a yellow solid: mp 176–177 °C (sealed capillary); IR (CCl_4) 1215 (N=Os), 925, 915 (Os=O) cm^{-1}; NMR ($CDCl_3$) δ 2.38 (m, 3, NCCCH), 2.18 (d, 6, J = 2 Hz, $NCCH_2$), 1.75 (t, 6, J = 2 Hz, $NCCCCH_2$).

Anal. Calcd for $C_{10}H_{15}NO_3Os$: C, 30.97; H, 3.90; N, 3.61. Found: C, 30.92; H, 3.80; N, 3.61.

Trioxo(2-methyl-2-butylimido)osmium(VIII) (6c). To a 200-mL recovery flask was added 5.0 g (19.6 mmol) of osmium tetroxide and 20 mL of olefin-free pentane. To the stirred solution was

added 2.30 mL (19.6 mmol) of *tert*-amylamine. After stirring for 5 min, the solvent was removed at reduced pressure to leave an orange-red mass which melted upon warming to room temperature. The product was stored in the dark, and 4 h later the liquid had resolidified to a yellow-brown mass. After standing overnight (18 h), it was sublimed (50–60 °C, 0.005 mm) to afford 5.54 g (87%) of yellow product: mp 60–61 °C (sealed capillary); IR (CCl_4) 1210 (Os=N), 930, 915 (Os=O) cm^{-1}; NMR ($CDCl_3$) δ 2.06 (q, 2, J = 6.5 Hz, CH_2), 1.66 (s, 6, $NCCH_3$), 1.10 (t, 3, J = 6.5 Hz, $NCCCH_3$).

Anal. Calcd for $C_5H_{11}NO_3Os$: C, 18.57; H, 3.43; N, 4.33. Found: C, 18.71; H, 3.70; N, 4.29.

Reaction of (*E*)-Cyclododecene with 6a (Bisulfite Workup). To a 50-mL round-bottom flask containing 10 mL of olefin-free methylene chloride, 0.122 g (0.395 mmol) of **6a**, and 0.019 g (0.09 mmol) of pentadecane was added 0.062 g (0.395 mmol) of (*E*)-cyclododecene. The reaction mixture was allowed to stir for 3 days before the methylene chloride was removed at reduced pressure. The residue was dissolved in 4.5 mL of pyridine, and a solution of 0.18 g of $NaHSO_3$ in 3 mL of H_2O was added. Stirring was continued for 24 h. The reaction mixture was then extracted with chloroform. The chloroform layers were combined and concentrated at reduced pressure, affording a brown oil which was acetylated with acetic anhydride/pyridine. The acetylated reaction mixture was analyzed by GLC on column B. The major peak was *threo*-1,2-diacetoxycyclododecane (40% yield). Because of the presence of an unidentified peak before the major one, a GLC–mass spectrum was obtained.[34] The substance was assigned the structure of 1-acetoxy-2-(*tert*-butylamino)cyclododecane based on its mass spectrum: *m/e* 297 [parent (P)], 282 (P − CH_3), 254 (P − Ac), 241, 199, 182.

Oxidation of 1-Decene with 6a in Methylene Chloride ($LiAlH_4$ Workup). After workup an aliquot was analyzed by GLC on column C. The results showed 62% of 1-(*tert*-butylamino)-2-decanol. A small sample of the reaction mixture was acetylated (acetic anhydride/pyridine) and analyzed by GLC on column A, which revealed the presence of 6% of 1,2-diacetoxydecane.

Oxidation of 1-Decene with 6a in Pyridine ($LiAlH_4$ Workup). After workup an aliquot was analyzed by GLC on column A and showed 89% of 1-(*tert*-butylamino)-2-decanol. Less than 1% of diol was observed.

Oxidation of 1-Decene with 6a in Pyridine (Bisulfite Workup). After workup the residue was dissolved in ethyl acetate and analyzed on GLC column A to show 78% of 1-(*tert*-butylamino)-2-decanol. When the same experiment was repeated a 75% yield of amino alcohol was obtained.

1-(*tert*-Butylamino)-2-decanol: Epoxide Opening. In a three-neck 500-mL flask fitted with an addition funnel, magnetic stirring bar, and reflux condenser and maintained under nitrogen was added 300 mL of anhydrous THF and 15.17 g (207 mmol) of *tert*-butylamine (distilled from CaH_2). The reaction flask was cooled in an ice bath, and 21.8 mL of 2.2 M methyllithium was added over a period of 5 min, resulting in vigorous evolution of methane. The mixture was stirred for 1 h before 5.0 g (32.1 mmol) of 1-decene oxide was added. The reaction mixture was refluxed for 24 h. TLC revealed complete consumption of epoxide. The reaction mixture was quenched with water and extracted twice with ether. The combined ether layers were washed with water and brine and then dried ($MgSO_4$). Removal of the solvent at reduced pressure gave 7.2 g of crude yellow oil. Distillation gave 4.1 g (75%) of clear oil (0.060 mm, 73.1–74 °C): IR (neat) 3200–3600 (broad assoc. OH), 1390, 1360 (*tert*-butyl), 1210 (C–N), 1180 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 3.5 (m, 1, –C**H**(OH)–), 2.5 (m, 4, OH, NH, $-CH_2N-$), 1.4–0.9 (m, 17, aliphatic $-CH_2-$, CH_3), 1.15 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{14}H_{31}NO$: C, 73.29; H, 13.62; N, 6.10. Found: C, 73.16; H, 13.53; N, 6.32.

The cyclic carbamate was prepared in a manner analogous to that described for the preparation of the carbamate of *erythro*-1-deuterio-1-(*tert*-butylamino)-2-decanol (see below): NMR ($CDCl_3$) δ 3.7 (t, 1, J = 7.5 Hz, NCH_2), 3.2 (t, 1, J = 7.5 Hz, NCH_2).

Preparation of 2-(*tert*-Butylamino)-1-decanol. A dry 500-mL three-neck round-bottom flask with vertical joints equipped with a mechanical stirrer, an addition funnel, a condenser capped with a drying tube, and a nitrogen inlet was charged with 23 mL (219 mmol) of *tert*-butylamine in 40 mL of dry ether. The reaction mixture was cooled in a dry ice–2-propanol bath maintained between −10 and −20 °C while a slight flow of nitrogen was maintained through the system. An 8 g (37 mmol) amount of 1-acetoxy-2-decanone[32] in 100 mL of dry ether was added quickly from the addition funnel. After rinsing the addition funnel with a small portion of ether, the nitrogen flow was increased and the addition funnel was charged with 2 mL (21 mmol) of titanium tetrachloride solution (1 M in hexane). The titanium tetrachloride solution was added over 40 min, and the addition funnel was rinsed with a small portion of ether. The brick red reaction mixture was gradually allowed to warm to room temperature while stirring for 1.5 h before it was quickly filtered through a fritted funnel. The solid was collected and washed with dry ether, the filtrate was dried (Na_2SO_4), and the solvents were removed at reduced pressure to afford a thick brown oil, presumably the *tert*-butylimine of 1-acetoxy-2-decanone.

In a dry, nitrogen-purged, 1-L three-neck round-bottom flask equipped with a mechanical stirrer, an addition funnel, and a reflux condenser was placed 2.8 g (74 mmol) of $LiAlH_4$ in 200 mL of dry ether. The system was maintained under a positive pressure of nitrogen, and the crude imine in 160 mL of dry ether was added from the addition funnel so as to maintain a gentle reflux. An additional 2.0 g (53 mmol) of $LiAlH_4$ was added, the reaction mixture was allowed to stir at ambient temperature overnight before it was cooled in an ice bath, quenched,[30] filtered, and dried (Na_2SO_4), and the ether was removed at reduced pressure to afford 5.98 g of a crude yellow oil. The product was purified by molecular distillation, and an analytical sample was obtained by preparative GLC on column D: IR ($CHCl_3$) 3405 (OH, NH, hydrogen bonded), 1395, 1368 (*tert*-butyl) cm^{-1}; NMR ($CDCl_3$) δ 1.12 (s, 9, *tert*-butyl).

1-Deuterio-1-decyne. To a 500-mL round-bottom flask was added 25 mL (0.138 mol) of 1-decyne and 200 mL of ether. The solution was maintained at −40 °C while 78 mL (2 M, 0.155 mol) of butyllithium in hexane was added over a 30-min period. The resulting white mixture was stirred at room temperature for 1 h before 20 mL of deuterium oxide was cautiously added. The ether became nearly colorless, and a white semisolid collected at the bottom of the flask. The ether was decanted, rinsed with 15 mL of dilute hydrochloric acid, 15 mL of saturated sodium bicarbonate, and 15 mL of brine, and dried (Na_2SO_4). The ether solution was concentrated and then distilled to afford 12.3 g (89%) of product: bp 170–176 °C; IR (neat) 2600 (CD) cm^{-1}; deuterium-decoupled NMR ($CDCl_3$) δ 2.20 (t, 2, J = 5 Hz, $C{\equiv}CCH_2$).

(*Z*)-1-Deuterio-1-decene. To a 250-mL round-bottom flask was added 12.3 g (0.088 mol) of 1-deuterio-1-decyne and 10 mL of hexane. An addition funnel was charged with 54 g (0.095 mol) of a 25% solution of diisobutylaluminum hydride in heptane, and the contents were slowly added to the flask over a 2-h period. The reaction mixture was then warmed to 45 °C, and the temperature was maintained for 3 h before the mixture was cannulated into an addition funnel fitted on a 1-L three-neck round-bottom flask equipped with a reflux condenser and a mechanical stirrer. To the flask was added 200 mL of pentane and 50 mL of distilled water. The contents of the addition funnel were slowly added to the rapidly stirred pentane/water emulsion over a 2-h period. The resulting mixture was allowed to stir overnight (10 h) before it was filtered, and most of the solvent was removed at reduced pressure. Distillation afforded 9.00 g (73%) of product: bp 165–169 °C; deuterium-decoupled NMR ($CDCl_3$) δ 5.78 (m, 1, CHD=C**H**), 4.88 (d, 1, J = 10 Hz, C**H**D).

(*E*)-1-Deuterio-1-decene was prepared analogously to the *Z* isomer from 1-decyne, but the vinylalkane was quenched with deuterium oxide: deuterium-decoupled NMR ($CDCl_3$) δ 5.83 (dt, 1, J = 6, 17 Hz, CHD=C**H**), 4.94 (dt, 1, J = 5, 17 Hz, C**H**D).

Oxyamination of (*E*)-1-Deuterio-1-decene with 6a in Methylene Chloride ($LiAlH_4$ Workup). To a 50-mL round-bottom flask was added 0.610 g (1.97 mmol) of trioxo(*tert*-butylimido)osmium-(VIII) (**6a**), 25 mL of methylene chloride, and 0.37 mL (1.9 mmol) of (*E*)-1-deuterio-1-decene. The solution turned black within seconds and was stirred in the dark under nitrogen for 2 days before the methylene chloride was removed at reduced pressure. To the black residue was added 25 mL of ether and 0.70 g of lithium aluminum hydride. The reduction mixture was stirred overnight (14 h) before it was quenched. Removal of the solvent at reduced pressure afforded the crude amino alcohol: NMR ($CDCl_3$) δ 1.10 (s, 9, *tert*-butyl).

The amino alcohol was dissolved in 30 mL of tetrahydrofuran, and 1.5 g (9.3 mmol) of carbonyldiimidazole was added. The solution was refluxed for 36 h before it was quenched with 25 mL of water and 300 mL of ether. The ethereal layer was washed with water (2 × 50 mL) and brine (50 mL) and dried (Na_2SO_4) before the solvent was removed at reduced pressure. The crude carbamate was purified by preparative TLC on silica gel eluting with 65% ethyl acetate in hexane. A second preparve TLC purification using 20% ethyl acetate in hexane then afforded pure product: deuterium-decoupled NMR ($CDCl_3$) δ 3.17 (d, 1, J = 7.5 Hz, C**H**D), 1.40 (s, 9, *tert*-butyl). The NMR spectrum also showed some of the all protio system and a small amount of the other deuterium isomer believed to be derived from nonspecific labeling of the 1-deuterio-1-decene.

Oxyamination of (*Z*)-1-Deuterio-1-decene in Methylene

Chloride with 6a ($LiAlH_4$ Workup). The procedure followed for the (*E*)-deuteriodecene was followed using 0.478 g (3.38 mmol) of (*Z*)-1-deuterio-1-decene. The crude amino alcohol was refluxed in 30 mL of tetrahydrofuran containing 3.5 g (22 mmol) of carbonyldiimidazole for 22 h. The product after workup was purified by preparative TLC on silica gel eluting with 20% ethyl acetate in hexane. Deuterium-decoupled NMR spectroscopy showed >95% of one deuterium labeled isomer as well as a small amount of the all proton compound: deuterium-decoupled NMR ($CDCl_3$) δ 3.65 (d, 1, J = 7.5 Hz, C**H**D). This isomer was identical with the one obtained by epoxidation of (*E*)-1-deuterio-1-decene with trifluoroperacetic acid[35] followed by epoxide opening with lithium *tert*-butylamide and carbamate formation with carbonyldiimidazole.

2-(*tert*-Butylamino)-1-phenylethanol by the Oxyamination of Styrene with 6a in Pyridine ($LiAlH_4$ Workup). After workup the product was bulb-to-bulb distilled (55 °C, 0.015 mm), affording a clear oil which crystallized from hexane to give 772 mg (74%) of white crystals: mp 87–88 °C (lit.[21] mp 86–87 °C); IR (CCl_4) 3400 (OH), 1390, 1365 (*tert*-butyl), 1220 (C–O), 1190, 1160, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (m, 5, aryl H), 4.6 (dd, 1, J = 4, 8 Hz, H–C–O), 2.75 (m 4, OH, NH, CH_2N), 1.1 (s, 9, *tert*-butyl).

1-(*tert*-Butylamino)-2-methyl-2-tridecanol by the Oxyamination of 2-Methyl-1-tridecene with 6a in Methylene Chloride ($LiAlH_4$ Workup). After workup an aliquot was analyzed by GLC on column A and showed 82% of 1-(*tert*-butylamino)-2-methyl-2-tridecanol and less than 1% of diol. 1-(*tert*-Butylamino)-2-methyl-2-tridecanol: IR (CCl_4) 3450 (OH), 1465 ($-CH_2-$), 1390, 1360 (*tert*-butyl), 1230 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 2.45 (s, 2, NCH_2), 3.0–2.0 (m, 2, NH, OH), 1.1 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{18}H_{39}ON$: C, 75.72; H, 13.77; N, 4.90. Found: C, 75.73; H, 13.48; N, 4.91.

1-(*tert*-Butylamino)-2-phenyl-2-propanol by the Oxyamination Oxidation of α-Methylstyrene with 6a in Methylene Chloride ($LiAlH_4$ Workup). After workup an aliquot was analyzed by GLC on column A and showed 93% of 1-(*tert*-butylamino)-2-phenyl-2-propanol: IR (CCl_4) 3410 (OH), 1600 (phenyl), 1390, 1360 (*tert*-butyl), 770, 700 (phenyl) cm^{-1}; NMR ($CDCl_3$) δ 7.4 (m, 5, aromatic H), 3.8 (AB q, 2, J = 12 Hz, $\Delta\nu_{AB}$ = 19.6 Hz, NCH_2), 1.45 (s, 3, HO–C–C**H**$_3$), 1.05 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{13}N_{21}NO$: C, 75.31; H, 10.21; N, 6.75. Found: C, 75.09; H, 10.00; N, 6.55.

1-(1-Adamantylamino)-2-phenyl-2-propanol by the Oxyamination of α-Methylstyrene with 6b in Methylene Chloride ($LiAlH_4$ Workup). After workup the crude product (1.2 g, brown oil) was converted to the amine hydrochloride by reaction with HCl in dry Et_2O and chromatographed on 90 g of silica gel eluting with a mixture of 58% ethyl acetate/40% hexane/2% triethylamine. The combined amino alcohol fractions were bulb-to-bulb distilled (79 °C, 0.1 mm), yielding 0.718 g (62%) of the white crystalline free amine: mp 65.5–67 °C; IR 3460 (OH), 1600 (NH), 1150 (C–O), 1100 (C–N), 700 cm^{-1}; NMR ($CDCl_3$) δ 7.4 (m, 5, aryl H), 2.8 (AB q, 2, J = 12 Hz, $\Delta\nu_{AB}$ = 14.7 Hz, $-NCH_2-C-OH$), 2.6–1.2 (m, 20, NH, OH, CH_3-C-OH, **adamantyl**-N).

1-(*tert*-Butylamino)-2-(4-cyanophenyl)-2-propanol by the Oxyamination of *p*-Cyano-α-methylstyrene with 6a in Pyridine (Bisulfite Workup). After workup the crude brownish black oil was chromatographed on 25 g of Florisil to afford 0.121 g (40%) of a clear oil which upon standing crystallized as a white solid: mp 48–49.5 °C; IR (CCl_4) 3400 (OH), 2875 (CH), 2240 (C≡N), 1390, 1365 (*tert*-butyl) cm^{-1}; NMR ($CDCl_3$) δ 7.55 (s, 4, aromatic H), 2.8 (AB q, 2, J = 12 Hz, $\Delta\nu_{AB}$ = 12 Hz, CCH_2N), 1.5 (s, 3, HO–C–C**H**$_3$), 1.1 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{14}H_{20}N_2O$: C, 72.37; H, 8.67; N, 12.06. Found: C, 71.90; H, 9.00; N, 11.95.

1-(*tert*-Butylamino)-2-(4-chlorophenyl)-2-propanol by the Oxyamination of *p*-Chloro-α-methylstyrene in Pyridine with 6a ($LiAlH_4$ Workup). After workup the crude product was bulb-to-bulb distilled (85 °C, 0.5 mm), affording 0.251 g (96%) of a clear oil: IR (neat) 3420 (OH), 1590 (phenyl), 1390, 1360 (*tert*-butyl), 1210 (C–N), 1090 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 7.35 (s, 4, aromatic H), 2.8 (AB q, 2, J = 12 Hz, $\Delta\nu_{AB}$ = 16 Hz, CCH_2N), 1.4 (s, 3, HO–C–C**H**$_3$), 1.05 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{13}H_{20}ClON$: C, 64.58; H, 8.34; N, 5.79. Found: C, 64.65; H, 8.46; N, 5.92.

1-(*tert*-Butylamino)-2-(4-methylphenyl)-2-propanol by the Oxyamination of *p*-Methyl-α-methylstyrene in Pyridine with 6a ($LiAlH_4$ Workup). After workup the crude product was chromatographed on 20 g of Florisil to afford 0.233 g (95%) a light yellow oil. The hydrochloride was prepared in ether as a white, powdery solid: mp 215.5–216 °C; NMR of the free amine ($CDCl_3$) δ 1.03 (s, 9, *tert*-butyl), 1.43 (s, 3, $OCCH_3$), 2.32 (s, 3, $CHCCH_3$), 2.75 (AB q, 2, J = 12 Hz, $\Delta\nu_{AB}$ = 18 Hz, NCH_2), 7.18 (A_2B_2 pattern, 4, J = 9 Hz, aryl H).

Anal. Calcd for $C_{14}H_{24}ClNO$: C, 65.21; H, 9.32; N, 5.43. Found: C, 64.91; H, 9.18; N, 5.31.

1-(*tert*-Butylamino)-2-(4-methoxyphenyl)-2-propanol by the Oxyamination of *p*-Methoxy-α-methylstyrene in Pyridine ($LiAlH_4$ Workup). After workup the crude product was chromatographed on 20 g of Florisil to afford 0.166 g (70%) of an oil. The hydrochloride was prepared as a white powder: mp 182–182.5 °C; NMR of the free amine ($CDCl_3$) δ 1.03 (s, 9, *tert*-butyl), 1.43 (s, 3, $OCCH_3$), 2.75 (AB q, 2, J = 12 Hz, $\Delta\nu_{AB}$ = 18 Hz, NCH_2), 3.76 (s, 3, OCH_3), 6.75 (A_2B_2 pattern, 4, J = 9 Hz, aryl H).

Anal. Calcd for $C_{14}H_{24}ClNO_2$: C, 61.41; H, 8.77; N, 5.12. Found: C, 61.12; H, 8.70; N, 5.28.

1-(*tert*-Butylamino)-2-(4-*N,N*-dimethylaminophenyl)-2-propanol by the Oxyamination of *p*-*N,N*-Dimethylamino-α-methylstyrene with 6a in Pyridine ($LiAlH_4$ Workup). Workup afforded 329 mg of straw-colored oil. Bulb-to-bulb distillation (85 °C, 0.02 mm) gave 279 mg of a clear oil. Spectral data (NMR) indicated that the yield of amino alcohol was 88% after correcting for the presence of 10% diol impurity: IR (CCl_4) 3440 (OH), 1610 and 1510 (aromatic C–H), 1390 and 1360 (*tert*-butyl) cm^{-1}; NMR ($CDCl_3$) δ 1.05 (s, 9, *tert*-butyl), 1.45 (s, 3, $OCCH_3$), 2.7 (AB q, 2, J = 12 Hz, $\Delta\nu_{AB}$ = 18 Hz, NCH_2), 2.9 (s, 6, NCH_3), 7.0 (A_2B_2 pattern, 4, J = 9 Hz, aryl H).

Oxidation of (*E*)-5-Decene with 6a in Methylene Chloride ($LiAlH_4$ Workup). After workup an aliquot was analyzed by GLC on column A and showed 20% of *threo*-6-(*tert*-butylamino)-5-decanol and 50% of *threo*-5,6-decanediol.

Oxidation of (*E*)-5-Decene with 6a in Pyridine ($LiAlH_4$ Workup). Analysis of the crude product after workup by GLC on column B showed 95% of *threo*-6-(*tert*-butylamino)-5-decanol and less than 3% of *threo*-5,6-decanediol.

***threo*-6-(*tert*-Butylamino)-5-decanol:** IR (CCl_4) 3350 (OH), 1470 ($-CH_2-$), 1390, 1365 (*tert*-butyl), 1230 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 3.1 (bs, 1, H–C–OH), 3.0–2.0 (m, 3, OH, NH, NCH), 1.15 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{14}H_{31}NO$: C, 73.29; H, 13.62; N, 6.10. Found: C, 73.42; H, 13.80; N, 5.93.

Oxidation of (*Z*)-5-Decene with 6a in Methylene Chloride: Isolated Yield ($LiAlH_4$ Workup). After workup, removal of the ether at reduced pressure afforded 0.94 g of a white crystalline solid whose spectral properties and R_f on boric acid treated TLC (35% ethyl acetate/hexane; R_f 0.56; authentic *threo*-5,6-decanediol has R_f 0.63) were identical with *erythro*-5,6-decanediol, 54% yield. The same reaction mixture was analyzed by GLC on column A and showed 53% of 5,6-decanediol. No amino alcohol was present.

Oxidation of (*Z*)-5-Decene with 6a in Pyridine at Room Temperature. The reaction mixture was stirred for 1 day followed by standard workup. Analysis of the reaction mixture by GLC on column A showed 42% of *erythro*-5,6-decanediol and 25% of *erythro*-6-(*tert*-butylamino)-5-decanol.

Oxidation of (*Z*)-5-Decene with 6a in Pyridine at 0 °C. The oxyamination was conducted at 0 °C, and the mixture was stirred for 6 days before the pyridine was removed under high vacuum. Octadecane was added as an internal standard, and the standard $LiAlH_4$ workup was used. Analysis of the reaction mixture by GLC on column A showed 65% of *erythro*-6-(*tert*-butylamino)-5-decanol and 22% of *erythro*-5,6-decanediol. Only 50% of the olefin had reacted after 3 days. The full 6 days were necessary for a high conversion to the products.

***trans*-2-(*tert*-Butylamino)-1-cyclohexanol.** To a 50-mL round-bottom flask fitted with a condenser and maintained under nitrogen was added 1.0 g of cyclohexene oxide (10.2 mmol), 6 mL of water, and 2.15 mL of *tert*-butylamine (20.5 mmol). The reaction mixture was refluxed for 24 h. A yellow-brown layer formed on top of the aqueous layer. The reaction mixture was partitioned between ether and water, and the water layer was extracted twice with ether. The combined ether layers were washed with brine, dried (Na_2SO_4), and evaporated to dryness, yielding 1.0 g of an off-white solid (57%), mp 47–48.5 °C. The amine hydrochloride was prepared in anhydrous Et_2O, mp 217.5–218.5 °C. The free amine analyzed on column C did not coinject with *cis*-2-(*tert*-butylamino)-1-cyclohexanol. The trans amino alcohol: IR (CCl_4) 3490 (OH), 1460 ($-CH_2-$), 1390, 1360 (*tert*-butyl), 1180 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 3.0 (m, 1, H–C–O), 2.0 (m, 3, OH, NH, HCN), 1.15 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{10}H_{21}NO$: C, 70.12; H, 12.35; N, 8.18. Found: C, 69.99; H, 12.34; N, 8.00.

***cis*-2-(*tert*-Butylamino)-1-cyclohexanol by the Oxyamination of Cyclohexene with 6a in Pyridine ($LiAlH_4$ Workup).** After

workup solvent removal yielded, without need of further purification, 127 mg of white crystals (88%), mp 79.1–81.4 °C. The amine hydrochloride was prepared in anhydrous ether, mp 213–214 °C. The amino alcohol: IR (CCl_4) 3450 (OH), 1400, 1360 (*tert*-butyl) cm^{-1}; NMR ($CDCl_3$) δ 3.6 (m, 1, -C**H**(OH)), 3.0–2.0 (m, 3, -CH(NR), OH, NH), 1.5 (s, 8, CH_2), 1.1 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{10}H_{22}ClNO$: C, 57.81; H, 10.67; N, 6.74. Found: C, 57.58; H, 10.8; N, 6.72.

***cis*-2-(1-Adamantylamino)-1-cyclohexanol by the Oxyamination of Cyclohexene with 6b in Pyridine ($LiAlH_4$ Workup).** After workup the solvent was removed at reduced pressure to afford 216 mg of a white crystalline solid (79%), mp 131–132 °C. The amine hydrochloride was prepared in anhydrous ether, mp 312 °C dec. The free amino alcohol: IR (KBr) 3450 (OH), 3100 (NH), 1100 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 3.5 (m, 1, H–C–O), 2.8 (m, 2, HCN, NH).

Anal. Calcd for $C_{16}H_{28}ClNO$: C, 67.22; H, 9.52; N, 4.90. Found: C, 67.06; H, 9.76; N, 4.80.

***cis-exo*-3-(*tert*-Butylamino)bicyclo[2.2.1]heptan-2-ol by the Oxyamination of Norbornene with 6a in Pyridine ($LiAlH_4$ Workup).** Chromatography of the crude product on silica gel afforded 224 mg (94%) of product. The hydrochloride was prepared in anhydrous ether: mp 203 °C; NMR of free amine ($CDCl_3$) δ 3.33 (d, 1, J = 6 Hz, OCH), 2.67 (d, 1, J = 6 Hz, NCH).

Anal. Calcd for $C_{11}H_{22}ClNO$: C, 60.12; H, 10.09; N, 6.37. Found: C, 59.74; H, 9.93; N, 6.40.

Oxyamination of 1,2-Dihydronaphthalene with 6a in Pyridine ($LiAlH_4$ Workup). The crude green oil was chromatographed on Florisil, and the combined amino alcohol fractions afforded a white solid (38%). The hydrochlorides were prepared in anhydrous ether. The amino alcohol fractions contained a mixture of the 1 and 2 cis regioisomers. The mixture of amine hydrochlorides: IR (KBr) 3300 (NH, OH), 2480 (NH_2^+), 1580 (aromatic, H, $N\overset{+}{N}H_2$), 1390, 1380 (*tert*-butyl), 1200 (C–O) cm^{-1}. *cis*-1-Hydroxy-2-(*tert*-butylamino)-tetralin: NMR ($CDCl_3$) δ 4.45 (d, 1, J = 5 Hz, ArC(**H**)OH), 1.25 (s, 9, *tert*-butyl). *cis*-1-(*tert*-Butylamino)-2-hydroxytetralin: NMR ($CDCl_3$) δ 3.95 (s, 1, ArCC(**H**)OH), 1.15 (s, 9, *tert*-butyl). The ratio of the 2-hydroxy isomer to the 1-hydroxy isomer is 69:31 as determined by GLC on column B.

Anal. Calcd for $C_{14}H_{22}ClNO$ (mixture of 1 and 2 regioisomers): C, 65.74; H, 8.67; N, 5.47. Found: C, 65.67; H, 8.74; N, 5.28.

Oxyamination of (*E*)-1-Phenylpropene with 6a in Pyridine ($LiAlH_4$ Workup). GLC analysis on column C showed that the crude product contained two compounds in a ratio of 76:24. The crude reaction mixture was chromatographed on Florisil, and the fractions were analyzed on column C. Fractions were obtained that contained the pure major isomer. This proved to be *threo*-1-(*tert*-butylamino)-1-phenyl-2-propanol by NMR analysis. The hydrochloride was prepared in ether as a white solid: mp 209–210 °C; NMR of free amine ($CDCl_3$) δ 1.02 (m, 12, *tert*-butyl and $OCCH_3$), 2.65–3.7 (m, 4, NH, OH, NCH, OCH), 7.23 (m, 5, aryl H).

NMR analysis of an additional fraction revealed an enrichment in the minor component (67%) which proved to be *threo*-1-phenyl-2-(*tert*-butylamino)-1-propanol, the regioisomer of the major product. The chemical shifts assignable to the minor component in the NMR spectrum of this mixture are δ 1.17 (*tert*-butyl) and 3.90 (d, J = 9 Hz, OCH).

The yield of the combined amino alcohol containing fractions was 91%. An analytical sample of the hydrochloride of a fraction which was an 80:20 mixture of the major and minor isomers was prepared in ether as a white solid.

Anal. Calcd for $C_{13}H_{22}ClNO$: C, 64.08; H, 9.04; N, 5.75. Found: C, 63.98; H, 8.82; N, 5.67.

Oxyamination of (*Z*)-1-Phenylpropene with 6a in Pyridine ($LiAlH_4$ Workup). GLC analysis on column C showed that the crude product contained two compounds in a ratio of 97:3. The crude reaction mixture was chromatographed on Florisil, and the fractions were analyzed by GLC on column C. Fractions were obtained that contained the pure major isomer, which proved to *erythro*-1-(*tert*-butylamino)-1-phenyl-2-propanol by NMR analysis. The hydrochloride was prepared as a white solid in ether: mp 198.5–200 °C; NMR of free amine ($CDCl_3$) δ 0.89 (d, 3, J = 6 Hz, $OCCH_3$), 1.07 (s, 9, *tert*-butyl), 7.28 (m, 5, aryl H).

Anal. Calcd for $C_{13}H_{22}ClNO$: C, 64.08; H, 9.04; N, 5.75. Found: C, 63.76; H, 9.10; N, 5.59.

NMR analysis of a fraction which was a 72:28 (minor isomer/major isomer) mixture of the two isomers revealed that the minor isomer was *erythro*-2-(*tert*-butylamino)-1-phenyl-1-propanol. Chemical shifts assignable to it in the NMR spectrum of the mixture are δ 1.17 (*tert*-butyl) and 4.58 (d, J = 4 Hz, OCH).

The combined weight of the fractions containing the pure amino alcohols was 0.29 g (92%).

Oxyamination of Citronellol Methyl Ether with 6a in CH_2Cl_2 ($LiAlH_4$ Workup). An NMR spectrum of the crude product showed diol as the sole product. The crude oil was chromatographed on 11.0 g of silica gel, yielding 171 mg (78%) of 2,6-dimethyl-8-methoxy-2,3-octanediol.

Oxyamination of Citronellol Methyl Ether with 6a in Pyridine. After workup an aliquot was analyzed on column A and showed a 38% yield of 3-(*tert*-butylamino)-2,6-dimethyl-8-methoxy-2-octanol and a 45% yield of 2,6-dimethyl-8-methoxy-2,3-octanediol.

3-(*tert*-Butylamino)-2,6-dimethyl-8-methoxy-2-octanol: IR (CCl_4) 3400, 1460 (–CH_2–), 1390, 1360 (*tert*-butyl), 1120 (C–O) cm^{-1}; NMR ($CDCl_3$) δ 3.35 (m and s, 5, CH_3–O–CH_2), 3.0–2.0 (m, 3, OH, NH, NCH–), 1.15 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{15}H_{33}NO_2$: C, 69.44; H, 12.82; N, 5.40. Found: C, 69.25; H, 12.77; N, 5.18.

1-(*tert*-Butylamino)-1-phenyl-2-methyl-2-propanol by the Oxyamination of 2-Methyl-1-phenylpropene with 6a in Pyridine. After workup the crude brownish oil was chromatographed on Florisil. The combined amino alcohol containing fractions were dissolved in dry ether. Hydrogen chloride was bubbled in, and 358 mg (88%) of white powder was collected: mp 214–215 °C; free amine, mp 62–63 °C. The amino alcohol hydrochloride: IR (KBr) 3300 (OH), 1560 (NH), 1390, 1380 (*tert*-butyl), 1190, 1160 cm^{-1}. The free amino alcohol: NMR ($CDCl_3$) δ 7.25 (s, 5, aryl H), 3.6 (s, 1, –CHN), 1.6–3.0 (m, 2, OH, NH), 1.15 (s, 3, CH_3), 1.0 (s, 12, *tert*-butyl, CH_3).

Anal. Calcd for $C_{14}H_{23}ON$: C, 75.97; H, 10.47; N, 6.33. Found: C, 75.81; H, 10.81; N, 6.19.

2-(*tert*-Butylamino)-1-phenylcyclohexanol by the Oxyamination of 1-Phenylcyclohexene with 6a in Pyridine ($LiAlH_4$ Workup). After workup the crude product was chromatographed on Florisil to afford a mixture of diol and amino alcohol. The products were dissolved in ether and washed with 2 × 20 mL of 1 N hydrochloric acid. The ether layer was dried (Na_2SO_4) and the solvent removed to afford 19 mg (8%) of diol. The aqueous extract was made basic by the addition of 10% sodium hydroxide and extracted with ether. The ethereal extracts were dried (Na_2SO_4), and the solvent was removed at reduced pressure to afford 202 mg (65%) of 2-(*tert*-butylamino)-1-phenylcyclohexanol. Although it has not been proved in this case, the vicinal amino and hydroxyl substituents are almost certainly cis to each other. The hydrochloride was prepared in anhydrous ether: NMR of the free amine ($CDCl_3$) δ 2.97 (m, 1, NCH), 0.78 (s, 9, $NCCH_3$).

2-(*tert*-Butylamino)-1-methylcyclopentanol by the Oxyamination of 1-Methylcyclopentene with 6a in Pyridine ($LiAlH_4$ Workup). The crude product was chromatographed on 20 g of Florisil to afford 140 mg (66%) of an oil which was determined to be one compound by GLC analysis; in this case too, the product is assumed to result from cis oxyamination. The hydrochloride was prepared as a white solid in ether: mp 220–220.5 °C (sealed capillary); NMR of the free amine ($CDCl_3$) δ 1.10 (s, 9, *tert*-butyl), 1.20 (s, 3, $OCCH_3$).

Anal. Calcd for $C_{10}H_{22}ClNO$: C, 57.85; H, 10.60; N, 6.75. Found: C, 57.86; H, 10.50; N, 6.68.

Reaction of Tetramethylethylene with 6a in Pyridine ($LiAlH_4$ Workup). The crude product was chromatographed on 25 g of silica gel and gave 239 mg (82%) of pinacol as a clear glass which crystallized upon standing. All spectral data were identical with that for authentic pinacol.

4-(*tert*-Butylamino)-1-phenyl-1,3-butanediol by the Oxyamination of 1-Phenylbut-3-en-1-ol with 6a in Pyridine ($LiAlH_4$ Workup). The product, a straw-colored oil, was chromatographed on Florisil to afford 177 mg (50%) of solid amino alcohol. The product was twice crystallized from hexane to afford an analytical sample: mp 105–106 °C; NMR ($CDCl_3$) δ 7.34 (m, 5, aryl H), 4.94 (t, 1, J = 6 Hz, aryl C**H**OH), 1.80 (t, 2, J = 6 Hz, HOCC**H**$_2$–COH), 1.10 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{14}H_{24}ClNO_2$: C, 61.41; H, 8.84; N, 5.12. Found: C, 61.55; H, 9.05; N, 5.02.

1-(*tert*-Butylamino)-3-phenoxy-2-propanol by the Oxyamination of Allyl Phenyl Ether in Pyridine ($LiAlH_4$ Workup). The product, a dark solid, was chromatographed on silica gel to afford 235 mg (70%) of a beige crystalline product. Crystallization from hexane/methylene chloride afforded an analytical sample: mp 95.5–97 °C; NMR ($CDCl_3$) δ 3.98 (m, 1, OCH), 3.00 (s, 1, OH), 2.78 (m, 2, NCH), 1.15 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{13}H_{21}NO_2$: C, 69.92; H, 9.48; N, 6.27. Found: C, 69.63; H, 9.65; N, 6.31.

1-(1-Adamantylamino)-3-phenoxy-2-propanol by the Oxyamination of Allyl Phenyl Ether with 6b ($LiAlH_4$ Workup). The product, a black oil, was chromatographed on silica gel to afford 236

mg (66%) of a glass which crystallized upon standing overnight. The product was dissolved in anhydrous ether, and hydrogen chloride was introduced to precipitate 221 mg (55%) of the amine hydrochloride as an eggshell-colored solid: mp 223–235 °C; NMR of free amine ($CDCl_3$) δ 3.95 (m, 1, OCH), 1.67 (s, 12, CCH_2C).

1-(2-Methyl-2-butylamino)-3-phenoxy-2-propanol by the Oxyamination of Allyl Phenyl Ether with 6c in Pyridine ($LiAlH_4$ Workup). The crude product was chromatographed on Florisil to afford 244 mg (88%) of a white crystalline solid. Crystallization from hexane afforded an analytical sample: mp 62.5–63.5 °C; NMR ($CDCl_3$) δ 3.95 (m, 1, OCH), 1.05 (s, 6, $NCCH_3$).

Anal. Calcd for $C_{14}H_{23}NO_2$: C, 70.85; H, 9.77; N, 5.90. Found: C, 70.52; H, 10.07; N, 5.79.

1-(*tert*-Butylamino)-3-thiophenoxy-2-propanol by the Oxyamination of Allyl Phenyl Sulfide in Pyridine with 6a ($LiAlH_4$ Workup). The crude product was chromatographed on Florisil eluting with chloroform and 1% triethylamine in chloroform to afford 173 mg (66%) of a pale tan oil. The hydrochloride was prepared in ether/methanol as a white powder: mp 104–105 °C; NMR of the free amine ($CDCl_3$) δ 3.68 (m, 1, OCH), 3.05 (d, 2, J = 6 Hz, SCH_2), 1.07 (s, 9, *tert*-butyl)

Anal. Calcd for $C_{13}H_{22}ClNOS$: C, 56.60; H, 8.04; N, 5.08. Found: C, 56.50; H, 8.30; N, 5.36.

1-(*tert*-Butylamino)-3-phenylamino-2-propanol by the Oxyamination of *N*-Allylaniline with 6a in Pyridine ($LiAlH_4$) Workup). The crude product, a black oil, was chromatographed on silica gel to afford off-white crystals (52%). Crystallization from hexane afforded an analytical sample: mp 90.5–92 °C; NMR ($CDCl_3$) δ 1.12 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{13}N_{22}N_2O$: C, 70.22; H, 9.98; N, 12.60. Found: C, 70.18; H, 9.66; N, 12.61.

1-(*tert*-Butylaminomethyl)-4-(*tert*-butyl)cyclohexanol: A. By the Oxyamination of 4-(*tert*-Butyl)methylenecyclohexane with 6a in Pyridine ($LiAlH_4$ Workup). Analysis of the crude reduction product by GLC on column A showed it to consist of an 81:19 mixture of the equatorial and axial alcohols by comparison with the authentic amino alcohols. The crude product was chromatographed on Florisil to afford 228 mg (93%) of a white product: NMR ($CDCl_3$) δ 2.53 (s, 2, NCH_2, axial), 2.35 (s, 2, NCH_2, equatorial), 1.08 (s, 9, *N*-*tert*-butyl), 0.87 (s, 9, C-4 *tert*-butyl).

Anal. Calcd for $C_{15}H_{32}ClNO$: C, 64.83; H, 11.61; N, 5.42. Found: C, 64.94; H, 11.37; N, 4.93.

B. By Epoxide Opening. To a 25-mL round-bottom flask was added 4.0 mL of *tert*-butylamine, 4.0 mL of distilled water, and 0.20 g (1.26 mmol) of an axial epoxide enriched mixture of the axial and equatorial epoxides of 4-(*tert*-butyl)methylenecyclohexane. The reaction was stirred at reflux for 36 h before the excess *tert*-butylamine was removed at reduced pressure. The resulting aqueous slurry was extracted with methylene chloride, the organic layer was dried (Na_2SO_4), and the solvent was removed, leaving a crude product which was chromatographed on Florisil to afford 206 mg (76%) of a mixture of amino alcohols. The major product from the epoxide opening corresponded to the minor product from the oxyamination and vice versa.

1-(1-Adamantylaminomethyl)-4-(*tert*-butyl)cyclohexanol by the Oxyamination of 4-(*tert*-Butyl)methylenecyclohexane with 6b in Pyridine ($LiAlH_4$ Workup). After workup, analysis of the crude white solid by GLC on column A showed an 81:19 ratio of isomers assigned as the equatorial and axial alcohols, respectively, by analogy to the *tert*-butylamino alcohol analogue. Chromatography on Florisil afforded 320 mg (91%) of product: NMR ($CDCl_3$) δ 2.58 (s, 2, NCH_2, axial), 2.40 (s, 2, NCH_2, equatorial), 0.87 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{21}H_{37}NO$: C, 78.93; H, 11.67; N, 4.38. Found: C, 79.12; H, 11.47; N, 4.42.

1-(2-Methyl-2-butylaminomethyl)-4-(*tert*-butyl)cyclohexanol by the Oxyamination of 4-(*tert*-Butyl)methylenecyclohexane with 6c in Pyridine ($LiAlH_4$ Workup). The crude product proved to be an 81:19 mixture of isomers by GLC analysis on column A. Chromatography on Florisil afforded 227 mg (81%) of an oil which slowly crystallized upon standing. The product was converted to the hydrochloride in anhydrous ether: NMR of free amine (CCl_4) δ 2.42 (s, 2, NCH_2, axial), 2.27 (s, 2, NCH_2, equatorial), 1.00 (s, 6, $NCCH_3$), 0.85 (s, 9, *tert*-butyl).

Anal. Calcd for $C_{16}H_{34}ClNO$: C, 65.83; H, 11.74; N, 4.80. Found: C, 65.66; H, 11.84; N, 4.68.

Reaction of OsO_4 with 4-(*tert*-Butyl)methylenecyclohexane: A. In Pyridine. To a 50-mL round-bottom flask was added 105 mg (0.689 mmol) of 4-(*tert*-butyl)methylenecyclohexane and 175 mg (0.689 mmol) of osmium tetroxide in 4.4 mL of pyridine. The reaction mixture was stirred for 36 h before the solvent was removed at reduced pressure, and 30 mL of ether was added followed by 388 mg of $LiAlH_4$. The reduction mixture was stirred overnight (17 h) before it was quenched to afford a mixture of diols (inseparable under all of the GLC conditions tried) as a white crystalline solid (mp 99–118 °C). The crude product was dissolved in methylene chloride, and part of the solution was transferred to a 50-mL round-bottom flask. Removal of the methylene chloride left 70 mg of crude product. To the 50-mL flask was added 75 mg (0.39 mmol) of *p*-toluenesulfonyl chloride and 1 mL of pyridine. The reaction mixture was stirred for 44 h before ice was added, after which it was stirred for an additional 30 min. The reaction mixture was taken up in 200 mL of ether and rinsed with water. The ether was dried ($MgSO_4$) and the solvent removed to afford a white crystalline solid. The crude monotosylate was dissolved in 15 mL of ether and reduced with 280 mg of $LiAlH_4$ at reflux for 1 h. Workup afforded a white crystalline solid which was 86% equatorial alcohol by GLC analysis on column A.

The assignment of the stereochemistry was confirmed by preparing a mixture of the two alcohols enriched in the axial alcohol from 4-(*tert*-butyl)cyclohexanone and methylmagnesium bromide.[33] A mixture of the two alcohols enriched in the equatorial alcohol was prepared by the lead tetraacetate oxidation of 4-(*tert*-butyl)methylenecyclohexane followed by a sequence of reactions identical with that used for the osmium tetroxide oxidations.[28] All GLC data were consistent with the assigned stereochemistries.

B. In Methylene Chloride. To a 50-mL round-bottom flask was added 203 mg (0.799 mmol) of osmium tetroxide, 4 mL of methylene chloride, and 122 mg (0.799 mmol) of 4-(*tert*-butyl)methylenecyclohexane. The reaction mixture was stirred for 36 h before the solvent was removed and ether added. The ethereal slurry was reduced with 525 mg of $LiAlH_4$ for 17 h. Workup afforded a white crystalline solid (mp 121–123 °C). The two diols were inseparable under all of the GLC conditions tested. The crude product was dissolved in methylene chloride, and part of the solution was transferred to a 50-mL round-bottom flask. Removal of the solvent left 80 mg of white solid. To the crude diol was added 85 mg (0.45 mmol) of *p*-toluenesulfonyl chloride and 1 mL of pyridine. The reaction mixture was stirred for 44 h before ice was added, and stirring was continued for 30 min. The reaction mixture was taken up in ether and rinsed with water. The ether was dried ($MgSO_4$) and the solvent removed at reduced pressure to afford a crystalline solid. The solid was dissolved in ether and reduced with 210 mg (5.5 mmol) of $LiAlH_4$ at reflux for 1 h. Workup afforded a white solid which was shown to be 82% equatorial alcohol by GLC analysis on column A.

Olefin Competition for Relative Rate Determinations. Relative rates for the various substituted olefins and para-substituted α-methylstyrenes were determined by competing one olefin against another in the presence of a deficiency of the oxidant and monitoring the *disappearance of the starting materials* by GLC. The GLC response factors for the two olefins were determined relative to a suitably chosen internal standard. The reactions were analyzed by GLC after being taken to roughly 50% total olefin conversion. The number of millimoles of each remaining olefin was calculated, and the relative rates were determined by using eq 3, in which A_f and B_f are the number of millimoles remaining of olefins A and B, respectively. A_0 and B_0 are the initial number of millimoles of olefins A and B, respectively. In all competitions that were conducted, a solution of the imidoosmium compound was added to a stirred solution of both olefins. The volume of both solutions was adjusted such that the combined solution was approximately 0.1 M with respect to the osmium reagent.

$$\frac{k_A}{k_B} = \frac{\log (A_f/A_0)}{\log (B_f/B_0)} \quad (3)$$

A description of the experimental conditions for the competition of (*E*)-5-decene and (*Z*)-4-octene follows. All of the other reactions were run in an analogous manner. For the sake of brevity, only the olefins that competed and the solvent employed for the oxyamination will be given for the remaining competitions.

Competition of (*E*)-5-Decene and (*Z*)-4-Octene. In a 10-mL round-bottom flask 36.0 mg (0.256 mmol) of (*E*)-5-decene and 28.0 mg (0.249 mmol) of (*Z*)-4-octene were dissolved in 1 mL of olefin-free methylene chloride. The solution was stirred, and 76 mg (0.245 mmol) of trioxo(*tert*-butylimido)osmium(VIII), **6a,** dissolved in 2 mL of olefin-free methylene chloride was added to the olefin solution. Undecane (38 mg, 0.243 mmol) was added to the reaction mixture as the internal standard. The reaction mixture was stirred for 24 h and subsequently analyzed by GLC on column A to show 0.19 mmol of (*Z*)-4-octene and 0.089 mmol of (*E*)-5-decene remaining. By applying

the equation given, $k((E)$-5-decene$)/k((Z)$-4-octene) was computed to be 4.22.

Remaining Competitions: k(styrene)/k(1-decene) = 2.1, CH_2Cl_2; k(1-undecene)/k(2-methyl-1-tridecene) = 2.6, CH_2Cl_2; k(1-dodecene)/k(α-methylstyrene) = 1.31, CH_2Cl_2; k(citronellol methyl ether)/k(z)-5-decene) = 2.9, CH_2Cl_2; k(2-methyl-1-tridecene)/k(2,3-dimethyl-2-octene) = 1.01, CH_2Cl_2; $k((E)$-1-phenyl-1-propene$)/k((Z)$-1-phenyl-1-propene) = 4.89, pyridine; k(phenyl allyl ether)/k(4-phenyl-1-butene) = 0.95, pyridine; k(p-N,N-dimethylamino-α-methylstyrene)/k(α-methylstyrene) = 1.63 (pyridine), 4.26 (CH_2Cl_2); k(p-methoxy-α-methylstyrene)/k(α-methylstyrene) = 1.49 (CH_2Cl_2), 1.04 (pyridine); k(p-methyl-α-methylstyrene)/k(α-methylstyrene) = 1.01 (pyridine), 1.14 (CH_2Cl_2); k(p-chloro-α-methylstyrene)/k(α-methylstyrene) = 1.23 (pyridine), 0.95 (CH_2Cl_2); k(p-cyano-α-methylstyrene/k(α-methylstyrene) = 1.53 (pyridine), 1.93 (CH_2Cl_2).

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Registry No.—6a, 50381-48-1; **6b,** 55946-71-9; **6c,** 63174-17-4; **9** (R = octyl), 55915-80-5; 11 (R = octyl), 55915-79-2; OsO_4, 20816-12-0; *tert*-butylamine, 75-64-9; 1-adamantylamine, 768-94-5; *tert*-amylamine, 594-39-8; *threo*-1,2-cyclododecanediyl diacetate, 65794-87-8; 1-acetoxy-2-(*tert*-butylamino)cyclododecane, 65760-92-1; 1,2-decanediyl diacetate, 60671-14-9; 1-decene oxide, 2404-44-6; 5-octyl-3-(*tert*-butyl)oxazolidin-2-one, 65760-93-2; 2-(*tert*-butylamino)-1-decanol, 65760-94-3; 1-acetoxy-2-decanone, 65760-95-4; 1-acetoxy-2-decanone *tert*-butylimine, 65760-96-5; 1-deuterio-1-decyne, 39650-97-0; 1-decyne, 764-93-2; (*Z*)-1-deuterio-1-decene, 39106-48-4; (*E*)-1-deuterio-1-decene, 39106-47-3; 1-deuterio-1-(*tert*-butylamino)-2-decanol, 65760-69-2; 1-(*tert*-butylamino)-2-(4-methylphenyl)-2-propanol HCl, 65760-70-5; 1-(*tert*-butylamino)-2-(4-methoxyphenyl)-2-propanol HCl, 65760-71-6; *threo*-5,6-decanediol, 58581-16-1; *erythro*-5,6-decanediol, 3266-25-9; *trans*-2-(*tert*-butylamino)-1-cyclohexanol, 65760-72-7; *trans*-2-(*tert*-butylamino)-1-cyclohexanol HCl, 65770-73-8; cyclohexene oxide, 286-20-4; *cis*-2-(*tert*-butylamino)-1-cyclohexanol HCl, 65760-74-9; *cis*-2-(1-adamantylamino)-1-cyclohexanol HCl, 65760-75-0; *cis-exo*-3-(*tert*-butylamino)bicyclo[2.2.1]heptan-2-ol HCl, 65760-76-1; *cis*-1-hydroxy-2-(*tert*-butylamino)tetralin HCl, 65760-77-2; *cis*-1-(*tert*-butylamino)-2-hydroxytetralin HCl, 65760-78-3; *threo*-1-(*tert*-butylamino)-1-phenyl-2-propanol HCl, 65760-79-4; *threo*-1-phenyl-2-(*tert*-butylamino)-1-propanol HCl, 65760-80-7; *erythro*-1-(*tert*-butylamino)-1-phenyl-2-propanol HCl, 65760-81-8; 2,6-dimethyl-8-methoxy-2,3-octanediol, 65760-61-4; 1-(*tert*-butylamino)-1-phenyl-2-methyl-2-propanol HCl, 65760-62-5; 2-(*tert*-butylamino)-1-methylcyclopentanol HCl, 65760-63-6; pinacol, 76-09-5; 4-(*tert*-butylamino)-1-phenyl-1,3-butanediol, 65760-64-7; 4-(*tert*-butylamino)-1-phenyl-1,3-butanediol HCl, 65760-65-8; 1-phenylbut-3-en-1-ol, 936-58-3; 1-(*tert*-butylamino)-3-phenoxy-2-propanol, 64980-40-1; allyl phenyl ether, 1746-13-0; 1-(1-adamantylamino)-3-phenoxy-2-propanol, 36144-08-8; 1-(1-adamantylamino)-3-phenoxy-2-propanol HCl, 40536-65-0; 1-(2-methyl-2-butylamino)-3-phenoxy-2-propanol, 65760-66-9; 1-(*tert*-butylamino)-3-thiophenoxy-2-propanol, 65760-67-0; 1-(*tert*-butylamino)-3-thiophenoxy-2-propanol HCl, 15148-93-3; allyl phenyl sulfide, 5296-64-0; 1-(*tert*-butylamino)-3-phenylamino-2-propanol, 65760-68-1; *N*-allylaniline, 589-09-3; 4-(*tert*-butyl)methylenecyclohexane, 13294-73-0; 4-(*tert*-butyl)methylenecyclohexane axial epoxide, 7787-78-2; 4-(*tert*-butyl)methylenecyclohexane equatorial epoxide, 18881-26-0; 4-(*tert*-butyl)-1-hydroxymethyl-1-cyclohexanol monotosylate (equatorial), 65760-60-3; 1-undecene, 821-95-4.

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