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Autoxidation of Trimethylamine in Aqueous Solutions[‡]

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The autoxidation of trimethylamine in aqueous solutions has been studied at 100 °C and at O_2 pressures up to 153 atm. Trimethylamine *N*-oxide is a major product. Its yield accounts for as much as, but never in excess of 50%, the balance being Me_2NH and $HCONMe_2$. The reaction follows second-order kinetics, $-d[Me_3N]/dt = k[Me_3N]P_{O_2}$, where $k = 8.7 \times 10^{-7}$ atm^{-1} s^{-1}. In solutions buffered with 0.1 N NaOH, the yield of Me_3NO is reduced. These results are interpreted in terms of a rate-limiting electron-transfer reaction between Me_3N and dioxygen, followed by reactions dictated by the radical ions, $Me_3N^{\bullet+}$ and $O_2^{\bullet-}$, thus generated. It is noted that only one oxygen atom in the O_2 molecule is incorporated into Me_3NO, the other being used in the sacrificial oxidations to give other products.

Introduction

Autoxidation of tertiary amines in the neat liquid or in organic solvents is generally believed to proceed by a radical chain mechanism similar to those for the autoxidation of hydrocarbons.[1-4] Oxidative dealkylation is the predominant pathway, and amine *N*-oxides have never been reported as products in these systems. However, in recent studies,[5-7] tertiary amine *N*-oxides were found in high yield when the autoxidation was carried out in aqueous solutions. At high O_2 pressures, production of the amine *N*-oxides in excess of 95% was reported for Me_3N and $Me_2(C_{12}H_{25})N$; the reaction is depicted in eq 1.[6,7] To

$$2R_3N + O_2 \rightarrow 2R_3NO \qquad (1)$$

account for this unprecedented stoichiometry, a new mechanism was proposed by Riley et al. According to this mechanism, the electron-transfer reaction between R_3N and O_2 is the rate-limiting step, which generates the aminium radical cation $R_3N^{\bullet+}$ and the superoxide ion $O_2^{\bullet-}$. Trapping of the aminium radical cation by O_2 gives $R_3NO_2^{\bullet+}$, which is then reduced by a second molecule of R_3N or $O_2^{\bullet-}$ to give the zwitterion ion, $R_3N^+OO^-$. The reduction of $R_3N^+OO^-$ by another molecule of R_3N yields R_3NO according to eq 1. In other words, in aqueous solutions and under high O_2 pressures, the commonly known radical chain mechanism is suppressed by the new reaction pathway, which leads to the production of amine *N*-oxides.

This latest report was a potential breakthrough for our ongoing pursuit for a system that efficiently uses molecular oxygen in catalytic organic synthesis in non-radical-chain pathways. Since tertiary amine *N*-oxides are known to be good oxidants for alcohols,[8] olefins,[9] carboxylic acids,[10] etc., and eq 2 has been found to be nearly thermal neutral,[11] a catalyst system using trimethylamine (or other tertiary amines) as a catalyst could, therefore, be developed according to eq 2 and 3, where S is an oxidizable substrate.

$$2Me_3N + O_2 \rightarrow 2Me_3NO \qquad (2)$$

$$Me_3NO + S \rightarrow R_3N + SO \qquad (3)$$

However, under similar conditions, we have not been able to reproduce the high yields described in the earlier report[6,7] for the autoxidation of trimethylamine. In our laboratories, Me_3NO was never produced in excess of 50%. Under the conditions we used, the reaction is more complicated than eq 2 depicts, and it appears that only one oxygen atom can be incorporated into Me_3NO, the other oxygen atom being used in the sacrificial oxidation to give other products. Our results are best interpreted in terms of a rate-limiting electron-transfer reaction between Me_3N and O_2, as proposed by Riley, followed by the chemistry of the aminium radical cation discussed by Beckwith.[5]

Table I. Oxygen Balance for the Autoxidation of Me_3N[a]

	Me_3N, mmol	Me_3NO, mmol	Me_2NH, mmol	HCO_2^-, mmol	O_2,[b] mmol
initial	61.2				89.6
final	8	26	13	17	50.2
difference	−53	26	13	17	−39.4

[a] Initial solution, 180 mL of 0.34 M Me_3N; reaction at 100 °C for 20 h with the initial P_{O_2} of 37 atm. The organic products were analyzed by $^{13}C\{^1H\}$ NMR. [b] Determined by mass spectral analyses.

Results

Stoichiometry. The stoichiometry of eq 2 requires that 0.5 mol of O_2 is used for each mole of Me_3N consumed and that Me_3NO is the only organic product. To examine how well eq 2 describes the autoxidation of Me_3N in aqueous solutions under high O_2 pressures, we have determined both the oxygen balance and organic products for this reaction. A solution (180 mL) of 0.34 M Me_3N was pressurized to 256 atm with a gas mixture of O_2 (9.7%), N_2 (6.7%), and Ar (83.6%). The solution was allowed to react at 100 °C for 20 h. Analyses of the products and the head gas are summarized in Table I. From the consumption of 53 mmol of Me_3N, the yields of Me_3NO, Me_2NH, and HCO_2^- were 26, 13, and 17 mmol, respectively. Although only 74% of Me_3N consumed is accounted for in this experiment, the consumption of 0.74 mol of O_2 per mol of Me_3N reacted and the production of Me_2NH and HCO_2^- clearly indicate that eq 2 does not adequately describe the

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Table II. Product Distribution in the Autoxidation of Trimethylamine in Aqueous Solutions[a]

expt. no.	P_{O_2}, atm	t, h	Me_3N,[b] mmol	$\Delta(Me_3N)$,[c] mmol	pH[d]	products, mmol: Me_3NO (%)[e]	Me_2NH	HCO_2^-	$HCONMe_2$	H_2CO	CO_2	H_2	yield, %[f]
1	153	3.0	15.4	13.7	8.31	6.4 ± 0.4[g] (47)	4.2	3.1	1.0		0.16	<0.1	85
2[h]	153	4.0	21.4	18.9	8.32	8.4 ± 0.5[g] (44)	5.4	4.4	1.2	0.2	0.77	0.3	79
3[i]	114	2.7	6.50	5.78	12.91	0.90 (16)	3.1	4.2	0	trace			79
4[i]	68	8.0	1.81	1.43	13.10	0.12 (8)	1.17	1.01	0	0			90
5[i]	68	5.8	1.72	1.36	13.09	0.14 (10)	1.01	1.68	0	0			85

[a] A Berghof Teflon reactor was used; T = 100 °C. [b] Initial. [c] Consumed. [d] Of the product solution. [e] Numbers in parentheses are percentage yield. [f] Combined yield of nitrogen-containing products. [g] Average of determinations of two independently prepared samples. [h] HC(O)NMeH ≤ 0.1 mmol. [i] Contains 0.10 N NaOH.

stoichiometry of the oxidation of trimethylamine under these conditions. Our conditions appear to differ from the earlier work only in amine concentration and reactor type. Slightly lower amine concentrations (≤0.34 M) than the lowest used by Riley et al. (0.5 M) were used in our study to avoid exceeding the lower explosion limit for Me_3N vapor in oxygen.[12]

The stability of Me_3NO has also been examined. No decomposition of Me_3NO was observed at 150 °C for 5 h under an argon atmosphere, although it decomposes at 200 °C with a half-life of 2.5 h. Me_3N accounts for about half of the product; CO_2, but not O_2, is also generated in the decomposition.

The possibility that the discrepancy between Riley's results and ours arose from the difference in the reactors used, a Teflon/glass reactor in Riley's study and a stainless steel reactor in our initial study, was then addressed. A magnetically stirred Teflon reactor was used for subsequent stoichiometric and kinetic studies. Table II summarizes the distribution of products of the autoxidation of Me_3N in the Teflon reactor. The last column indicates that over 79% of the nitrogen-containing products have been accounted for in these experiments. In experiments 1 and 2, the reactions were carried out at its natural pH and Me_3NO is indeed a major product; however, it accounts for less than half of the Me_3N consumed. The combined yield of Me_2NH and $HCONMe_2$ was as high as 38%. Neither $MeNH_2$ nor HCONMeH was detected. As expected, HCO_2^-, CO_2, and H_2CO were also produced. The sum of these products accounts for the missing methyl group in the oxidative dealkylation of Me_3N to yield Me_2NH.

The yields of Me_3NO for the three experiments described (49, 47, and 44%, respectively) are all close to, but never exceed, 50%. These results, together with the consumption of 0.75 mol of O_2 per mole of Me_3N and the production of Me_2NH and HCO_2^-, suggest that the overall reaction is best described by eq 4, rather than eq 2.

$$2Me_3N + {}^3\!/_2O_2 \rightarrow Me_3NO + Me_2NH_2^+ + HCO_2^- \quad (4)$$

In experiments 3–5, the solutions were buffered with 0.1 N NaOH. Under these conditions, Me_2NH was the major product and Me_3NO only accounted for ~10% of the product.

Kinetics. The kinetics of the autoxidation of Me_3N has also been briefly examined. An initial solution of 6.5 × 10^{-3} M Me_3N was used, and the reaction was studied at 100 °C and at pressures of 34–136 atm. Since the rate and the pH fell off during the reaction in unbuffered solutions, presumably because of the production of HCO_2H, the rates were measured in solutions buffered with 0.10 N NaOH.

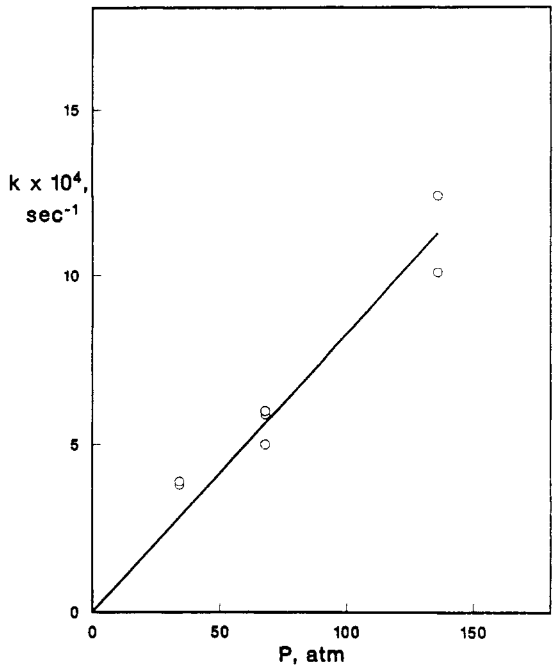

Figure 1. Rate of autoxidation of Me_3N as a function of O_2 pressure ($[Me_3N]_i = 6.5 \times 10^{-3}$ M, [NaOH] = 0.10 M, and T = 100 °C).

The reaction was followed by the disappearance of Me_3N. The rates of formation of Me_2NH and HCO_2^- parallel that of the disappearance of Me_3N. For prolonged reaction, the concentration of Me_2NH reached a maximum and then decreased, attributable to further oxidation of Me_2NH.

At constant oxygen pressure, the reaction followed pseudo-first-order kinetics for about 2 half-lives and then became slower. The pseudo-first-order rate constants were derived from the first 2 half-lives of the plots and are plotted against the O_2 pressure in Figure 1, from which the second-order rate constant k is calculated as 8.7 × 10^{-7} atm^{-1} s^{-1}.[13]

$$-d[Me_3N]/dt = k[Me_3N]P_{O_2} \quad (5)$$

Such second-order kinetics has also been reported by Riley et al.[6,7] for dimethyldodecylamine for which an activation energy of 19.1 kcal/mol has been reported.[14]

Discussion

We have shown that our results for the autoxidation of Me_3N at its natural pH are best described by eq 4, which

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(12) *IMC Methylamines: A Complete Guide.* International Minerals Chemical Co., 1979.

(13) The data clearly demonstrates the rate dependence on O_2 pressure. However, more data are needed to establish how well eq 5 is followed.

(14) This is considerably lower than the energy gap of 1.12 V (or 26 kcal) calculated from the reduction potential of O_2 and the peak potential for *N,N*-dimethyldodecylamine.[6] The authors attribute this difference to the uncertainty of the oxidation potential of *N,N*-dimethyldodecylamine. The activation energy for eq 6 has not been evaluated. However, assuming a preexponential factor of 10^{11} mol^{-1} s^{-1}, an activation energy of 22 kcal/mol is calculated.

suggests that only one oxygen atom of O_2 can be incorporated into Me_3NO. The other O atom is used in the sacrificial oxidation of the methyl group of Me_3N to yield Me_2NH and HCO_2^-. A 50% yield of Me_3NO has been reported by Weil and Mahr[15] in the dye-sensitized autoxidation of Me_3N in aqueous solutions. In that study, a consumption of 1 mol of O_2 per mole of Me_3N has also been reported. In the autoxidation of *N*-methylpyrrolidine in aqueous solutions, a 40% yield of *N*-methylpyrrolidine *N*-oxide has been reported by Beckwith and co-workers.[5]

The reported high yield of Me_3NO in excess of 95% has led Riley et al. to come to the conclusion that the autoxidation of Me_3N in aqueous solutions under moderate oxygen pressures follows eq 2. It is noted here that the selectivity for Me_3NO is 91.3% in the limiting "sacrificial oxidation" type reaction shown in eq 6, in which only 50%

$$23Me_3N + 21O_2 \rightarrow 21Me_3NO + 9H_2O + CO_2 + N_2 \tag{6}$$

of the consumed oxygen is incorporated into Me_3NO. Therefore, the selectivity for Me_3NO production alone is not a good criterion for establishing the stoichiometry of eq 2. It is imperative that the oxygen balance and the nitrogen balance are also examined.

It is not warranted to discuss in length the mechanism for the autoxidation of trimethylamine with the limited data we have. For the purpose of understanding our results, a simplified mechanism is formulated in Scheme I, which adopts the rate-limiting electron-transfer reaction (eq 7) suggested by Riley,[6] and the aminium radical cation chemistry proposed by Beckwith[5,16] for the autoxidation of *N*-methylpyrrolidine in aqueous solutions. The sum of eq 7–14, with eq 10 doubled, yields eq 4.

Scheme I

$$Me_3N + O_2 \xrightarrow{\text{r.d.s.}} Me_3N^{\bullet+} + O_2^{\bullet-} \tag{7}$$

$$Me_3N^{\bullet+} \rightarrow Me_2NCH_2^{\bullet} + H^+ \tag{8}$$

$$Me_2NCH_2^{\bullet} + O_2 \rightarrow Me_2N^+{=}CH_2 + O_2^{\bullet-} \tag{9}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^{\bullet} \tag{10}$$

$$2HO_2^{\bullet} \rightarrow H_2O_2 + O_2 \tag{11}$$

$$Me_2N^+{=}CH_2 + H_2O \rightarrow Me_2NH_2^+ + H_2CO \tag{12}$$

$$H_2CO + \tfrac{1}{2}O_2 \rightarrow HCO_2^- + H^+ \tag{13}$$

$$Me_3N + H_2O_2 \rightarrow Me_3NO + H_2O \tag{14}$$

In strongly alkaline solutions, eq 14 is slower because of the deprotonation of H_2O_2, resulting in the lower yield of Me_3NO. Presumably, HO_2^- accumulates under these reaction conditions.

An alternative to eq 9 is eq 15 and 16, which are chain propagation reactions in a radical-chain process. Similarly, the hydroperoxy radical, instead of disproportionating as shown in eq 11, may initiate radical-chain reactions, according to eq 17. These radical reactions, predominating

$$Me_2NCH_2^{\bullet} + O_2 \rightarrow Me_2NCH_2O_2^{\bullet} \tag{15}$$

$$Me_2NCH_2O_2^{\bullet} + Me_3N \rightarrow Me_2NCH_2O_2H + Me_2NCH_2^{\bullet} \tag{16}$$

$$HO_2^{\bullet} + Me_3N \rightarrow Me_2NCH_2^{\bullet} + H_2O_2 \tag{17}$$

in the autoxidation of amines in nonpolar organic solvents, apparently are not favored in aqueous solutions. Inclusion of these radical reactions would change the kinetics, as well as the stoichiometry of the reaction.

The rate-limiting electron-transfer reaction in eq 7 apparently is so slow in nonpolar solvents that most of the autoxidation reaction of amines in these solvents were studied with the aid of a radical initiator. The initiation step is also slow and difficult to study in aqueous solutions at atmospheric pressures.[5] The second-order rate law, eq 5, observed at elevated O_2 pressures in Riley's and in our studies, lends support to the conclusion that eq 7 is rate-limiting in our system, and that radical-chain reactions are not important under our reaction conditions. Consistent with this conclusion, Beckwith reported that neither the radical initiators nor the acceptors affect the rate of autoxidation of *N*-methylpyrrolidine. However, the reaction is accelerated by electron acceptors and retarded by electron donors.[5]

The formation of $HC(O)NMe_2$ may derive from further oxidation of Me_2NCH_2OH. Absence of $HC(O)NMe_2$ in solutions of 0.1 N NaOH may simply be due to its hydrolysis (eq 18).

$$HC(O)NMe_2 + OH^- \rightarrow HCO_2^- + Me_2NH \tag{18}$$

Experimental Section

Materials. Anhydrous Me_3N (Aldrich) and HPLC-grade H_2O (Alltech) were used without further purification. Oxygen (CP) and certified gas mixtures blended from CP gases were from Matheson.

Instruments. The following instruments were used in this study: Varian FT-80 NMR, Varian 3700 GC, Orion 901 Ionalyzer, Berghof 500-mL Teflon autoclave equipped with a magnetic stirrer and gas- and liquid-sampling devices, and Autoclave Engineer's 300-mL autoclave.

Analyses. These analyses apply to the results shown in Table II. Me_3N, Me_2NH, $MeNH_2$, $Me_2NC(O)H$, and $MeHNC(O)H$ were analyzed on a 6-ft × $^1/_8$-in. column of 4% Carbowax and 0.8% KOH on Graphpac GB with a flame ionization detector with the following program: 50° (10 min) to 220° (30 min) at 10° per min. Decomposition of Me_3NO to give Me_3N and Me_2NH was negligible at the injector temperature of 150 °C or lower. This was established by comparing the analyses of samples without workup and samples from which Me_3NO had been removed by vacuum distillation. HCHO was analyzed on a 10-ft × $^1/_8$-in. Porapak T column with a thermal conductivity detector with the program: 150° (3 min) to 200° to 10° per min.

Me_3NO was analyzed by its ^1H NMR spectrum. The samples were prepared by careful vacuum distillation of the solvent and other volatiles, followed by dissolution of the residue in D_2O. An attempt to analyze Me_3NO with reverse-phase HPLC on a C-18 column was not successful in our hands. Because of the weak UV absorption of Me_3NO, the presence of HCO_2^- and other products made its analysis difficult. In addition, the retention time of Me_3NO was found to be sensitive to the medium and changed from sample to sample.

HCO_2^- was analyzed by IR spectroscopy by its ν_{CO} band at 1607 cm^{-1}. CO_2 and H_2 in the head gas were analyzed on a 3.5-ft × $^1/_8$-in. Spherocarb column isothermally at 70 °C with argon as the carrier gas and with a thermal conductivity detector. For analysis of the dissolved CO_2, a sample was treated with concentrated HCl in a septum vial and the liberated CO_2 was analyzed by GC as described.

Autoclave Experiments. All the experiments shown in Table II and Figure 1 were carried out on the Berghof reactor, which was slightly modified by shortening the stirring shaft (which houses the thermal couple) for better temperature control. A solution of desired composition was prepared and loaded into the autoclave, which was then sealed. The reactor was then brought to the desired temperature. For stoichiometric studies presented in Table II, except for experiment 1, no sample was taken during the run and the product analyses were carried out on samples taken from the cold reactor at the end of the reaction. For kinetic studies, samples were taken at various times and analyzed.

Oxygen Balance. The reaction in Table I was carried out on the Autoclave Engineer's stainless steel autoclave. A solution of

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[15] Weil, L.; Maher, J. *Arch. Biochem. Biophys.* **1950**, *29*, 241.

[16] For an extensive review on Nonaromatic Aminium Radicals, see: Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243.

61.2 mmol of Me_3N in 180 mL of H_2O was heated at 100 °C for 20 h with an initial pressure (room temperature) of 17.7 atm of N_2, 29.3 atm of O_2, and 208.8 atm of Ar. Samples of the head gas were taken before and after the reaction and were analyzed by mass spectroscopy. The analyses of O_2 and N_2 were also confirmed by GC on a 10 ft molecular sieve column. N_2 was added as an internal standard for the analysis of O_2 by G.C. The results are shown in the table below.

	O_2	N_2	Ar	CO_2	H_2
before reaction[a]	9.6 (±0.3)	6.6 (±0.4)	82.6 (±0.8)	0	<0.02
after reaction	5.5 (±0.3)	7.3 (±0.4)	87.0 (±0.8)	0.011	0.1

[a] The balance is Me_3N.

The organic products were determined by $^{13}C\{^1H\}$ NMR spectroscopy. The IR spectra of the head gas also indicate the absence of N_2O, NO, and NO_2.

Deoxygenation of Me_3NO. A preliminary experiment indicates that no reaction occurs if an aqueous solution of Me_3NO (0.5 M) is heated first at 100 °C for 19 h and then at 150 °C for 5 h under 500 psi of argon atmosphere.

An aqueous solution of 0.92 M Me_3NO (160 mL) was heated at 200 °C and 500 psi of argon atmosphere. Samples were taken and analyzed by $^{13}C\{^1H\}$ NMR spectroscopy. Me_3NO disappeared with a half-life of 2.5 h; Me_3N accounted for about half of the product. At the end of the reaction, CO_2, but not O_2, was found in the sample of the head gas.

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Registry No. Me_3N, 75-50-3; Me_3NO, 1184-78-7; Me_2NH, 124-40-3; $HCONMe_2$, 68-12-2.

Steric Control of Epoxidation by Carbamate and Amide Groups. Evidence for the Carbonyl-Directed Epoxidation

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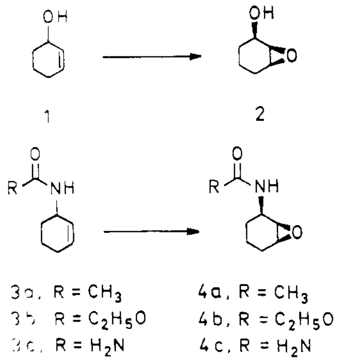
Allylic and homoallylic carbamoyloxy groups show a pronounced syn stereodirecting effect on peroxy acid epoxidation similar to that of hydroxy groups (**5** → **8**). Carbonyl oxygen of the ambident carbamoyloxy group has been found to be responsible for this steering. A similar effect operates in olefinic amides (**64** → **66**).

The hydroxyl-directed epoxidation of allylic alcohols (**1** → **2**; Scheme I) has evolved into a reliable and highly stereoselective method for the construction of vicinal chiral centers.[1-3] A similar syn directing effect has been found for amido[4] (**3a**), urethano[5] (**3b**), and ureido olefins[6] (**3c**) and for unsaturated acetals,[7] sulfones,[8] and sulfoxides[9,10] both in the aliphatic and alicyclic series. In contrast, epoxidation of esters[1,11] and carbonates[5g,12] of allylic alcohols proceeds either nonstereoselectively or produces predominantly *trans*-epoxides, while β,γ-unsaturated carboxylic acids afford mixtures of both cis and trans products.[13] In preliminary communications, we have described the syn epoxidation of various carbamates derived from allylic and homoallylic alcohols.[14,15] In this paper we report on the scope of this stereocontrolled epoxidation and discuss its mechanism.

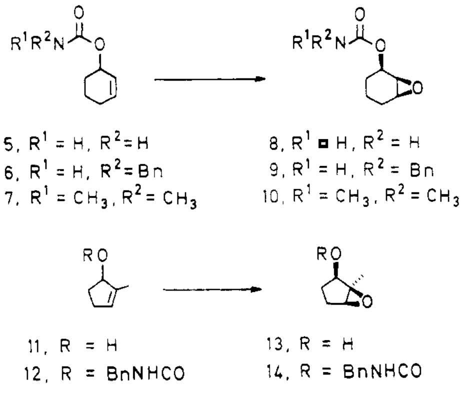
Results and Discussion

As a part of a broader program aimed at developing novel stereo- and regioselective methods by employing neighboring groups to control addition reactions,[16] we have now investigated the stereochemistry of epoxidation of allylic (**5–7**, **12**, **16**, **17**, **22**, **28**, and **34**) and homoallylic (**48–50**) carbamates.[17] We have found that carbamate **5**, *N*-benzylcarbamate **6**, and *N,N*-dimethylcarbamate **7**, derived from cyclohexenol (Scheme II), are predominantly oxidized with *m*-chloroperoxybenzoic acid (MCPBA) in noncoordinating solvents (such as CH_2Cl_2 or $CHCl_3$) at 0 °C in a syn fashion to afford *cis*-epoxides **8–10**, respectively, as the major products (Table I). Cyclopentenol **11** and its *N*-benzylcarbamate **12** follow the same pattern. The configuration of the epoxides thus obtained was es-

Scheme I



Scheme II



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