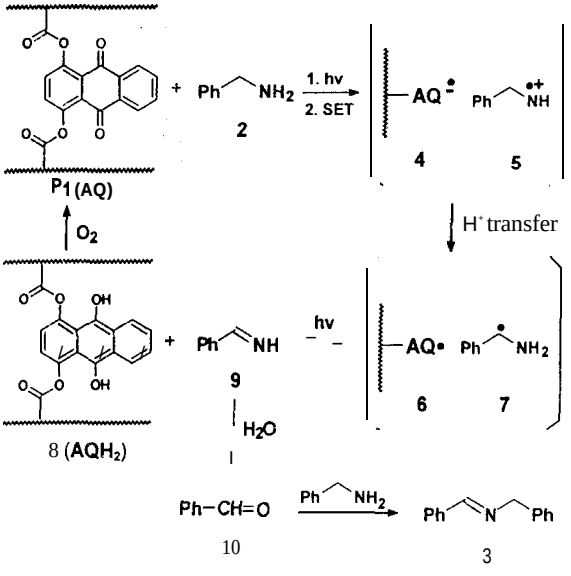

Scheme 4

transfer to generate the reduced dihydroxyanthracene 8 (AQH_2) and benzylimine 9. The reduced anthraquinone AQH_2 earr be oxidized to the starting AQ by molecular oxygen. 'fire benzylimine 9 then is hydrolyzed by water in the media to benzaldehyde 10 followed by condensation with benzylamine yielding the observed final product, *N*-benzylidenebenzylimine 3.

In this study, anthraquinone-containing, cross-linked polymers have been applied to oxidation of benzylamine. Benzylamine was readily oxidized to benzaldehyde by the polymers upon irradiation widr UV light. Since cross-linked polymer photocatalysts have unique advantages over small molecule catalysts, the results of this study might be useful in the development of new polymer photocatalysts. Application of the polymers to oxidation of secondary and tertiary amines is under progress.

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Diastereoselective Synthesis of Aryloxazinones

Seung-Han Lee* and Sung-Won Nam

Department of *Chemistry,* College of Natural Science, *Kyung* Hee *University, Yongin* 449-701, Korea
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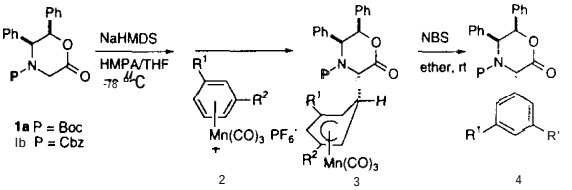
An interesting and important nonproteinogenic class of amino acids are the arylglycines.[1] One of the best-studied and most interesting sources of arylglycines are the glycopeptide antibiotics. However, the arylglycines are difficult to synthesize in optically pure form due to the ease at which the α-methine proton can undergo base-catalyzed racemization.[2]

Numerous approaches to the asymmetric synthesis of arylglycines have appeared, including: asymmetric Strecker synthesis;[3] arylation or alkylation of nucleophilic glycinates;[4] arylation of electrophilic glycinates;[5] electrophilic amination of chiral enolates;[6] and nucleophilic amination of α-substituted acids,[7] amongst others.[8]

We report herein our preliminary studies on the conversion of $(arene)Mn(CO)_3^+$ complexes to aryloxazinones, which can be converted to arylglycines, via their reaction with the Williams chiral glycine enolate equivalent (la or lb).[9]

$(Arene)Mn(CO)_3^+$ complexes (2) were treated with enolate of la or lb to give the substituted cyclohexadienyl-$Mn(CO)_3$ complexes (3) with high diastereoselectivity. We tried to separate the cyclohexadienyl-$Mn(CO)_3$ complexes, but significant decomposition of cyclohexadienyl-$Mn(CO)_3$ complexes occurs upon attempted silica gel chromatography. So direct treatment of these reaction mixture with *N*-bromosuecinimide effected oxidative demetallation[4a,4b,10] to give the aryloxazinones (4) in moderate yield and high di-



Scheme 1

Table 1. Arylation of Oxazinones Using (Arene)Mn(CO)$_3$ Complexes

Entry	P	Mn complexes	Product	Yield (%)	de (%)'
1	Boc	R^1=R^2=H	4a	59	90
2	Boc	R^1=H, R^2=OCH_3	4 b	65	89
3	Boe	R^1=R^2=OCH_3	4C	**50**	**85**
4	Cbz	R^1=R^2=H	4d	**59**	**88**
5	Cbz	R^1=H, R^2=OCH_3	**4e**	**66**	89
6	Cbz	R^1=R^2=OCH_3	4f	62	86

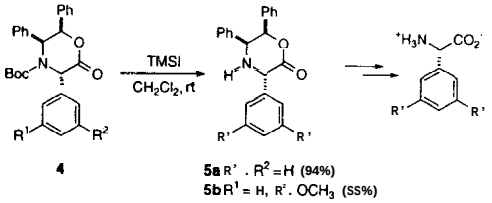
[a] Isolated chemical yields for anti-isomers. [b] % des determined from isolated yields.

astereoselectivit y (Scheme 1).

The results were summarized in Table 1. We have examined various bases (NaHMDS, LiHMDS, KHMDS, and n-BuLi) and found that NaHMDS (sodium bis(trimethylsilyl) amide) (1.8 equiv) gives the best results. In the absence of HMPA, the reaction gave the same products but lower yields. The addition of HMPA (THF/HMPA, 10: 1) improves the chemical yields. The electrophile approaches from the less hindered face of the oxazinone enolate giving the *anti*-oxazinone. At ambient temperature, the oxazinones are in SIOW confirmational exchange on the NMR time scale due to restricted rotation of the carbamate bond providing the two sets of the peaks. At higher temperature (DMSO-d_6, 373 K), the peakes collapse to give the sharp peaks. The stereochemistry of the phenyloxazinone **4a** ($[\alpha]_D$ − 78.2°) was determined by comparison with the known enantiomer of **4a** (lit.[5d] $[\alpha]_D$ +78.2°). In contrast to *anti*-oxazinone, *syn*-oxazinone provides the sharp NMR peaks to show the fast confirmational exchange at ambient temperature. Also, the syrr-aryloxazinone was prepared from the epimerization of the *anti*-aryloxazinone (NaHMDS/THF, -- 78 "C).

Removal of the Boc group with trimethylsilyl iodide in dichloromethane proceeds cleanly to give the (3*S*,5*S*,6*R*)-2,3,5,6-tetrahydro-3,5,6-triphenyl-l,4-oxazin-2-one (5)" (Scheme 2).

The following procedure is representative. Under a nitrogen atmosphere, to a stirred solution of la (0.16 g, 0.45 mmol, 1 equiv) in THF (10 mL) and HMPA (1 mL) was added NaHMDS (0.82 mL, 0.82 mmol, 1.8 equiv, 1.0 M solution in THF) dropwise via syringe at - 78 "C. After 40 rein, solid (η^6-benzene)tricabonylmanganese hexafluorophosphate (2) was added and the mixture was stirred at -78 "C for 1 h, quenched rapidly with aqueous ammonium chloride at - 78 "C, and extracted with diethyl ether. The ethereal solution was dried over $MgSO_4$, filtered, and stirred with NBS (81 mg, 0.45 mmol, 1 equiv) for 30 min at room temperature. The reaction solution was washed successfully with aqueous sodium hydrogensrrlfite, water, and brine, and was dried ($MgSO_4$). Evaporation of solvent, followed by flash chromatography (CH_2Cl_2 : n-Hex: EtOAc, 20:20: 1) allowed separation of the diastereomeric products (4).'[2]



4 **5a** R' . R^2 = H (94%)
5b R^1 = H, R^2. OCH_3 (SS%)

Scheme 2

In conclusion, the aryloxazinones were prepared in moderate yields and high diastereoselectivity from the nucleophilic substitution of chiral glycine enolate equivalents with (arene)Mn(CO)$_3^+$ complexes. Investigations concerning the conversion of aryloxazinones to arylglycines are underway.

Acknowledgment. We **are grateful to** the Korea Science and Engineering Foundation (92-25-00-08) and Kyung Hee University for financial suffort of this work. This paper is dedicated to Professor Sang Chul Shim on the occasion of his 60th birthday.

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11 (3 ***S,5S,6R*)-2,3,5,6-Tetrahydro-3,5,6-triphenyl-1,4-oxazin-2-one** (5a): This compound'. was identifed by comparison with the known enantiomer of **5a**.[5d] 1 H NMR (300 MHz, $CDCl_3$, 298 K) δ 2.35 (br s, 1H),. 4.72 (d, *J*=4.1 Hz, lH), 5.22 (s, lH), 5.71 (d, *J*=4.1 Hz, 1 H), 6.92-7.63 (m, 15 H). IR (KBr): 3374, 1748, 1214 cm '.
12. (3 ***S,5S,6R*)-4-(*tert*-Butyloxycarbonyl)-2,3,5,6-tetra**-hydro-3,5,6-triphenyl-l,4-oxazin-2-one (4a): mp 217-219 'C; $[\alpha]_D$ -78.2 (c 1, CH_2Cl_2); IR (KBr): 3075, 1748, 1692, 1451, 1386, 1234 cm '. 'H NMR (300 MHz, $CDCl_3$, 298 K) δ [1.13 (s), 1.27 (s), 9H], [5.19 (d, *J*=2.7 Hz), 5.45 (s), 1H], [5.76 (d, *J*=2.8 Hz), 5.85 (s), lH], [6.19 (s), 6.42 (s), lH], 6.72-7.59 (m, 15 H). For syrr-oxazinone: ^{1}H NMR (300 MHz, $CDCl_3$, 298 K) δ 1.19 (s, 9H), 5.71 (s, lH), 5.86 (d, *J*=2.9 Hz, lH), 6.07 (d, *J*=3.0 Hz, 1H), 6.95-6.98 (m, 2H), 7.19-7.29 (m, 13 H).

Oxidative Decarboxylation of Carbamates by Thianthrene Cation Radical

Young Sook Park, Dong Sul Han, and Wang Keun Lee*

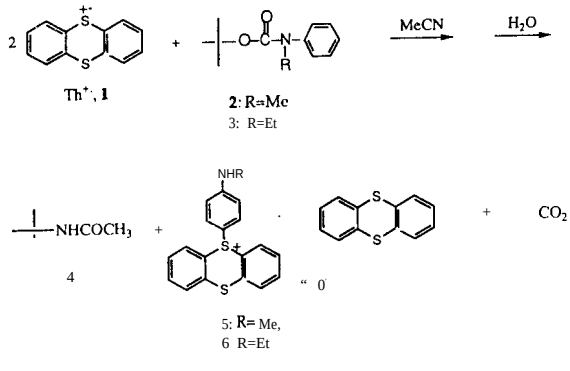
Department of Chemistry *Education, Chonnam* National *University, Kwang-Ju* 500-757, Korea
Received March *3*, 1998

Cation radical induced oxidative decompositions have attracted wide attention in recent years.[1-4] For example, azoalkane such as 1, 1'-azoadamantane (AA), was oxidized by thianthrene cation radical perchlorate ($Th^{+}\cdot ClO_4^-$, 1) in MeCN affording N_2 evolution with C,N bond cleavage.' In this 2:1 stoichiometry reaction of cation radical salts to AA adamantyl cation derived product was observed instead of product formed by free radical reaction. But, in the reaction of *tert*-butyl phenyl carbonate ($Me_3COCOOPh$) with 1, CO_2 was produced with C,O bond cleavage.[4] While adamantyl radicals formed from the first oxidation of AA were again oxidized imo adamantyl eations, phenoxy radicals formed from the oxidative decomposition of carbonate were not oxidized but trapped by 1 to give 5-substituted thianthreniumyl perchlorate salts.

We report here the first observation of electron-transfer-mediated C,N and C,O bond activation in stable carbamates. The stoichiometry for oxidative fragmentation of carbamate requires at least 2 mol equiv of cation radical to fully consume 1 mol of carbamate. All of the results that follow can be understood on the basis that *tert*-butyl cation and amine radical were trapped by solvent nitrile and cation radical respectively.

Chemical oxidation of carbamates, *tert*-butyl *N*-methylphenyl[5] (2) and *tert*-butyl *N*-ethylphenyl carbamate[5] (3), by 1 in MeCN yields C,N and C,O bond cleavage products (Scheme 1). The major products were *N-tert*-butylacetamide (4) from *tert*-butyl cations and 5-substituted thianthreniumyl perchlorates, 5-(4-*N*-methylaminopheny l)- (5) and 5-(4-*N*-ethyl-aminopheny l)thianthreniumyl perchlorate (6), from amine radicals respectively along with thianthrene (Th) and CO_2. Average product balances account for 72% of the tert-butyl groups which appear as cations, 84% of the amine radicals, and 86% of the cation radicals as determined by quantitative GC and GC/MS analyses, In addition to reduced oxidant Th, a small amounts (O. 1 %) of thianthrene 5-oxide (ThO) was also obtained.' These products and their yields are listed in Table 1.

The decarboxylation of carbamates has not very well known. The *tert*-butoxy carbonyl (Boc) group is removed by treating the protected amino acid or peptide with anhydrous acid,[7] such as trifluoroacetic acid or hydrogen chloride in acetic acid, base,[8] and catalysts.' The initial reaction



Scheme 1