Figure 2. The ^{13}C NMR spectrum of $[NiL^3](ClO_4)_2$ in Me_2SO-d_6 solution with solvent peaks omitted.

or CH_3CN ligands in the axial position to give octahedral species (see Figure 1) as is frequently observed with macrocyclic tetra-aza nickel(II) complexes. The reason might be due to the steric crowding of the axial sites increased by N-ethyl groups on two nitrogen atoms. The electronic spectra of Ni(II) and Cu(II) complexes of L^3 show the 6-7 nm shift of λ_{max} longer wavelengths than those of L^2, indicating that N-ethyl complexes weaken the ligand field strength of complex further than N-methyl complexes do[6]. Two nitrogen atoms with R_2(ethyl group) in L^3 tend to form sp^2 rather than sp^3 hybridization as suggested by the X-ray data of the Ni-N bonds length in similar complexes[9]. The ^1H NMR spectrum[10] of $[NiL^3](ClO_4)_2$ in Me_2SO-d_6 solution shows a sharp singlet at $\delta=2.08$ ppm which is assigned to the imine methyl groups. The methyl triplet and methene quartet of N-ethyl occur at $\delta=1.15$ and $\delta=2.74$ ppms, respectively. The three peaks mentioned just before as well as other ones do not show any broadening, indicating that this complex maintains the square-planar geometry and is diamagnetic even in coordinating solvent of Me_2SO[11].

The ^{13}C NMR spectrum of $[NiL^3](ClO_4)_2$ is shown to be 8 resonances rather than 16 ones, indicating that the ligand contains eight pairs of nonequivalent carbon atoms (Figure 2). This observation supports the symmetric arrangements of this complex. Namely, there is the possibility of two stereoisomers, *i.e.*, one N-meso form and the other racemic form[12]. We are currently doing X-ray analysis in order to tell in which form the complex exists. In conclusion, we have synthesized N-ethyl 14-tetra-aza diene (L^3) by the non-template reaction and its Ni(II) and Cu(II) complexes.

Acknowledgement. This work was supported by a grant from the Korea Research Foundation and the Basic Science Research Program, the Ministry of Education, Korea.

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5. **$L^3 \cdot 2HClO_4$**: Aqueous $HClO_4$ (70%, 0.1 mol) was added dropwise to ice-salt cooled solution of N-ethyl-1,2-diaminoethane (0.1 mol) in 60 m*l* methanol. After completion of the addition, but-3-en-2-one (0.1 mol) in 12 m*l* methanol was added drop by drop in ice bath. The mixture was then stirred for 2 hr in the ice bath. The white precipitate was filtered, and washed with methanol and diethyl ether (Yield 20%). The product was not stable, and then was used *in situ* for the following reaction without further purification.
6. **$[ML^3](ClO_4)_2$**: M(II) acetate and **$L^3 \cdot 2HClO_4$** were dispersed in methanol. The suspension was heated under reflux with stirring for *ca.* 2 hr and then cooled to room temperature. The precipitate was filtered, washed with methanol and diethyl ether, and recrystallized from 90% methanol. Elemental analysis. Calcd for **$C_{16}H_{32}N_4Ni(ClO_4)_2$**: C, 35.8; H, 6.0; N, 10.4%. Found: C, 35.3; H, 6.1; N, 10.2%. Yield: 65%; ^{13}C NMR (δ Me_2SO-d_6): 6.87, 22.86, 36.40, 46.02, 47.74, 51.44, 54.20, 184.75 Calcd for **$C_{16}H_{32}N_4Cu(ClO_4)_2 \cdot 1.5H_2O$**: C, 33.7; H, 6.2; N, 9.8%. Found: C, 33.9; H, 6.2; N, 9.6%; Yield 50%.
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α-Methylenelactam Synthesis *via* Radical Cyclization of Propiolamide

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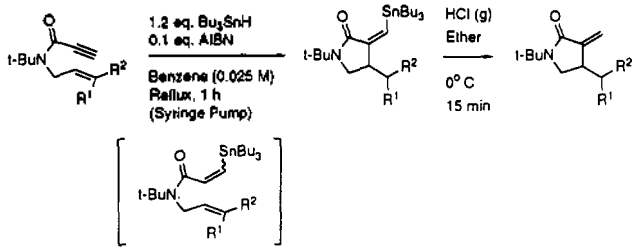
Received March 19, 1993

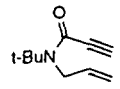
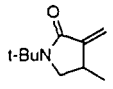
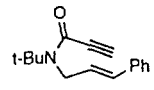
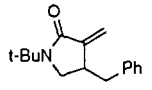
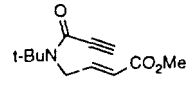
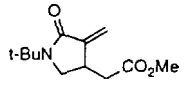
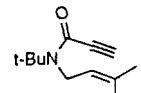
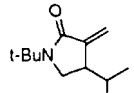
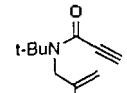
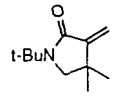
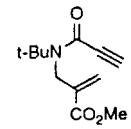
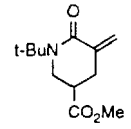
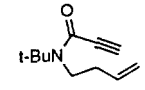
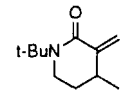
Lactam synthesis *via* cyclization of radicals generated from N-substituted haloacetamides is now well documented. Typically, N-allyl and N-propargyl haloacetamides undergo cyclization under various radical-generating conditions to afford γ-lactams.[1] Synthesis of β-lactams from N-vinyl haloacetamides was also reported.[2] These reactions proceed *via* (aminocarbonyl)methyl radical intermediates. In view of the results we obtained in the synthesis of α-methylenelactones and α-methylencycloalkanones from propiolates and acetylenic ketones[3] *via* (α-alkoxycabonyl-β-stannyl)vinyl and (α-carbonyl-β-stannyl)vinyl radicals, N-substituted propiolamides appeared to be proper substrates in the synthesis of α-methylenelactams. We now report that *t*-butyl-substituted N-allyl propiolamides indeed serve well as precursors in radical cyclizations *via* (α-aminocarbonyl-β-stannyl)vinyl radicals formed by the addition of stannyl radicals to the propiolamide triple bonds.

N-*t*-Butyl propiolamide was prepared from propiolyl chloride[4] and *t*-butylamine and it was reacted with various allylic bromides under basic conditions (KOH/DMSO)[5] to form substrates **1a-g**. Radical cyclization of these substrates was



Scheme 1.

Table 1.

Substrates	Products	Yield
 1a	 2a	43%
 1b	 2b	63%
 1c	 2c	95%[a]
 1d	 2d	73%
 1e	 2e	63%[b]
 1f	 2f	52%
 1g	 2g	48%

[a]Destannylation in HCl-MeOH. [b]Tributylstannane addition time: 3 h.

achieved under standard high-dilution conditions and the product α-stannylmethylenelactams[6] were destannylated under acidic conditions (Scheme 1). Substrates with N-allyl and 3-substituted allyl substituents were converted into α-methylene-γ-butyrolactams **2a**, **b**, **c**, and **d**, in reasonable yields (Table 1). These are products of *5-exo* cyclization and no *6-endo* cyclization products were isolated. The highest yield was achieved with the substrate **1c**, which suggest that the (α-aminocarbonyl-β-stannyl)vinyl radicals are nucleophilic. N-Methallyl derivative **1e** was converted into the *5-exo* cyclization product **2e** whereas the substrate **1f** yielded only the *6-endo* cyclization product **2f**. It should be reminded that methallyl propiolate is known to cyclize mainly in the *6-endo* mode.[3c] Finally, 3-butenyl derivative **1g** was transformed into the α-methylene-δ-valerolactam **2g** *via 6-exo* cyclization.

The results show that properly substituted propiolamides[7] are reasonable substrates in the radical cyclization producing eventually α-methylenelactams. The scope and utility of these cyclization reactions will be the subjects of our future investigations.

Acknowledgement. Authors thank the Ministry of Education, Republic of Korea, (BSRI-91-314), the Organic Chemistry Research Center (KOSEF) and Ukong Corporation for financial support.

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6. In all cases, predominant formation of (*Z*)-α-stannylmethylenelactams was evident from the characteristic NMR signals of the protons at δ 6.2-6.3.
7. No cyclization products were obtained from substrates lacking N-*t*-butyl substituent.