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(glycol and catalytic amount of *p*-toluenesulfonic acid in benzene), we were not able to get the desired compound in acceptable yield. After many failure, a reaction using trichloroacetic acid as a catalyst gave rise to 90% yield. We assumed that steric hindrance caused by methyl group at C-4 position required more drastic conditions. Before functionalizing B-ring, a carboethoxy group was converted to an angular methyl group by reduction, tosylation and substitution. In this substitution sequence, other derivatives were able to synthesize. Tosylation of the resulting alcohol 7 was also required a harsh condition because of 1, 3 diaxial interaction caused by methyl group at C-4 and hydrogens.

With all necessary carbons in place, B-ring was functionalized by allylic oxidation using Salmond procedure.[7] Treatment of compound 8 with chromium trioxide, Celite and 3,5-dimethylpyrazole under anhydrous condition afforded a key compound 9 in 63% yield. Addition of isopropylmagnesium chloride in THF followed by deketalization gave rise to the target compound in 38% yield. The spectral properties of this compound were in accordance with those reported.[3a]

In conclusion, we synthesized the β-cyperone 3 in 7 steps. Key steps are 1) Robinson annulation to construct a carbon skeleton 2) introduction of an angular methyl group at C-10 position 3) addition of isopropyl group by Grignard reaction followed by subsequent acidic hydrolysis to generate dienone moiety. This result will pave the way to prepare valuable starting materials from simple carbon skeletons. The development of synthetic routes for natural products and biologically active materials utilizing an octalone system are under investigation.

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Electron Transfer Process of Phenoxide Ion and α,β-Unsaturated Carbonyl Compounds

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Nucleophilic substitution catalyzed by single electron trasfer (=S.E.T) process, *i.e.,* occurring along with a $S_{RN}1$ mechanism,[1] is now a well-known reaction. The electron transfer process has been proposed to proceed *via* various manners; electrochemically,[2] photochemically,[3] or by metal ions.[4] A large variety of nucleophiles has been demonstrated to react with aliphatic[5] or aromatic[6] nitro substrates *via* $S_{RN}1$ processes. It has also been found that alkyl radicals derived from alkyl mercury halide undergo Michael 1,4-addition reactions with α,β-unsaturated carbonyl compounds *via* single electron transfer process.[7] It is noteworthy that phenoxide and alkoxide ions do not seem to react as nucleophiles with α,β-unsaturated carbonyl compounds, Recently, Thiebault *et al.* have studied electron transfer initiated chain reaction of phenoxide ion under electrochemical conditions. They found phenoxy radicals derived from electrochemical electron transfer process of phenoxide ion were cross-coupled with halosulfonyl compounds, halopyridine, and 4-halobenzophenone *via* $S_{RN}1$.[8]

We wish to report our preliminary results that 2,6-di-*tert*-butyl phenoxy radical derived from the corresponding phenoxide ion reacts with α,β-unsaturated carbonyl compounds to produce Michael 1,4-addition adduct, 1, as a major product and the dimer, 2, of the phenoxy radical as a minor product. The results are summarized in Table 1[9] and plotted in Figure 1.
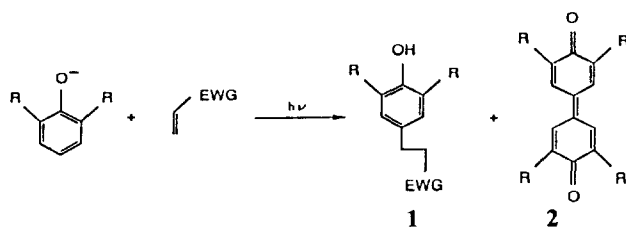

As shown in Table 1 and Figure 1, addition of 5 mole% of di-*tert*-butyl nitroxide or *m*-dinitrobenzene has shown a strong inhibitory effect on the final yield of Michael adduct and the dimer. In addition, either the presence of O_2 or the absence of UV inhibits the formation of Michael adduct. The bubbling of O_2 in the presence or the absence of methyl acrylate increases the formation of dimer, indicating that molecular oxygen would be the oxidant[10] in this reaction. The illumination of the reaction mixture with 254 nm or 350 nm UV light does not show a significant effect on the

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Table 1. Summary of the Reaction of 2,6-di-*tert*-Butylphenoxide Ion with Various α,β-Unsaturated Carbonyl Compounds in DMSO at 35℃

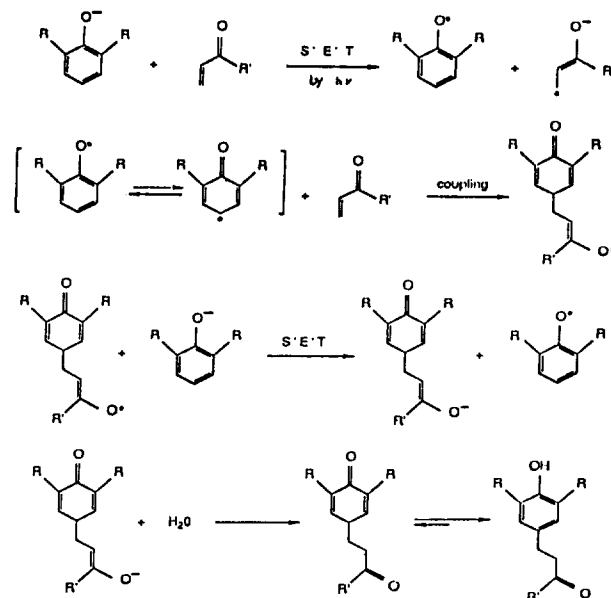| Conditions		Yields,[a] %	
		1	2
Methyl acrylate	UV[b], 8 h	80[e]	11[e]
Methyl acrylate	UV, 5 mol% DBN[c], 12 h	14	5
Methyl acrylate	UV, 5 mol% *m*-DNB[c], 12 h	55	3
Methyl acrylate	dar, 24 h	38	7
Methyl acrylate	O₂, 12 h	2	57
Methyl acrylate	AgNO₃[d], 24 h	87	10
Methyl vinyl ketone	UV, 10 h	31	8
Acrylonitrile	UV, 10 h	43	7

[a] Determined by GLC by the internal standard method. [b] Irradiation was performed with Rayonet photoreactor (254 nm or 350 nm) equipped with merry-go-round and cooling fan. [c] DBN = di-*tert*-butyl nitroxide, *m*-DNB = *m*-dinitrobenzene. [d] 1.1 eq of AgNO₃ was employed. [e] Isolated by flash column chromatography and confirmed with authentic sample by ¹H-NMR and GLC analysis.
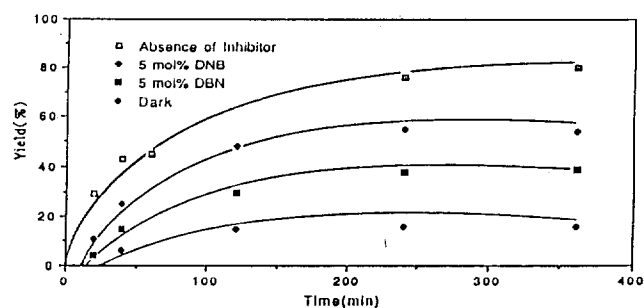
Figure 1. Plots showing the inhibitory effects *vs.* reaction time on the yield %.

Scheme 1.

electron transfer of phenoxide ion wherein the follow-up reaction is considered to involve a radical addition to α,β-unsaturated carbonyl compound followed by a further electron transfer to yield enolate. And the simplicity of the procedure make this an especially valuble synthetic method.

product yield. From these classical inhibition experiments,[11] we suggest that the phenoxy radical generated from single electron transfer process of phenoxide ion by photostimulation reacts with methyl acrylate, as shown in Scheme 1.

And, oxidation of phenoxide ion with AgNO₃ in the presence of methyl acrylate gave Michael adduct (87%) and dimer (9%) without UV-light. The phenoxy radical is generated by the Ag⁺ oxidation of phenoxide ion and this result clearly shows that phenoxy radical and methyl acrylate react by radical addition. Kaplan *et al.*[12] reported that AgNO₃ is a useful reagent for the oxidation of carbanion to generate radical. With Ag⁺ initiated reaction in the absence of α,β-unsaturated carbornyl compound, it is possible to raise the yield of the dimer product up to 85%, which renders the radical dimerization reaction attractive. The formation of dimer strongly indicates that the phenoxy radical is involved as an intermediate and is dimerized by free radical non-chain process.[13]

These results are reminiscent of the mechanism for the

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9. General procedure: The phenoxide is generated from phenol (1 mmol) by *t*-BuOK (1.1 mmol) in DMSO in a quartz tube and the substrate (1 mmol) is added under N₂. After consumption of the substrate, d-HCl is added and the extraction is carried out by CH₂Cl₂ after addition of water. UV stimulation by a Rayonet photoreactor (254, 350 nm) equipped with merry-go-round and cooling fan.
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Table 1. Spectral Data of Ni(II) and Cu(II) Complexes of L³

| Compound | IR spectra, cm⁻¹ | | d-d band^a | Reference |
	v(C=N)	v(ClO₄)	λ_{max}, (ϵ)^b	
[NiL²](ClO₄)₂	1650		448(111)	4
[NiL³](ClO₄)₂	1650	1092, 624	455(134)	this work
[CuL²](ClO₄)₂	1650		526(179)	4
[CuL³](ClO₄)₂	1663	1107, 625	532(207)	this work

^{a}In H₂O solutions at 25℃. ^{b}nm (dm³mol⁻¹cm⁻¹)

Synthesis of Nickel(II) and Copper(II) Complexes with Macrocyclic Ligand: 1,8-Diethyl-5, 12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4, 11-diene(L³)

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The reaction of the monohydroperchlorate salt of 1,2-diaminoethane with but-3-en-2-one in methanol solution gives the dihydroperchlorate salt of the macrocyclic ligand, 5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene (L¹)¹. This synthesis is an extension of the procedure devised by Curtis² for the preparation of the macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra-azacyclotetradeca-4,11-diene. However, most macrocycles³ obtained by Curtis method have no substitutes at the nitrogen atoms. Miyamura⁴ first reported the N-methyl tetra-aza macrocycle (L²) by the non-template reaction, but no further N-alkyl 14-tetra-aza diene macrocycles have been reported.

In this paper, we report the synthesis of the new macrocycle 1,8-diethyl-5,12-dimethyl-1,4,8,11-tetra-azacyclotetradeca-4, 11-diene (L³) by the non-template reaction of but-3-en-2-one with N-ethyl-1,2-diaminoethane hydroperchlorate salt and its Ni(II) and Cu(II) complexes.

L¹:R₁=Me
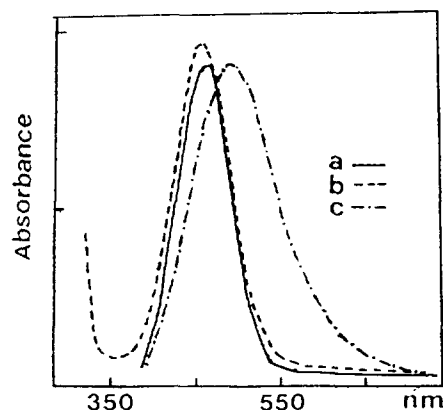
L²:R₁=R₂=Me, R₃=H
L³:R₁=Me, R₂=Et, R₃=H
L⁴:R₁=R₃=Me, R₂=Et
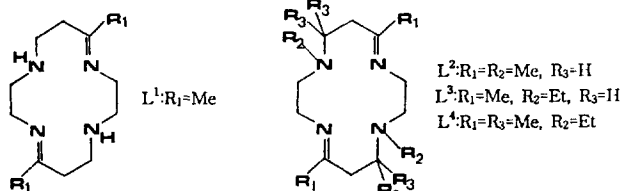
We could not obtain the macrocycle (L⁴) from the reaction of 4-methyl-3-penten-2-one with N-ethyl-1,2-diaminoethane. We suspect that it may be attributable to the effect of steric hindrance of the starting materials on the formation of the macrocycle (L⁴). A new ligand (L³) without having such a problem of streic hindrance might be readily obtained by reaction (Eq. 1) of but-3-en-2-one with N-ethyl-1,2-diaminoethane hydroperchlorate⁵. The ligand was, however, turned out to be unstable and decomposed within a few hours of

Figure 1. Visible absorption spectra of (a) [NiL³]²⁻ in CH₃NO₂, (b) [NiL³]²⁺ in CH₃CN, and (c) [CuL³]²⁺ in CH₃NO₂ at 25℃. [Notice the absence of the characteristic octahedral Ni(II) band of around 350 nm in CH₃CN solution.]

its isolation at room temperature. Its instability was only managed to be prevented us from doing analytical, IR or NMR measurements. Thus, the analysis for the ligand was performed on its Ni(II) and Cu(II) complexes. The latters were prepared and isolated as their perchlorate salts according to Eq. 2 as shown⁶;

$$2CH_3CH_2NHCH_2CH_2NH_2HClO_4 + 2CH_2CHCOCH_3$$
$$\longrightarrow L^3 \cdot 2HClO_4 \qquad (1)$$

$$L^3 \cdot 2HClO_4 + M(II) \longrightarrow [ML^3](ClO_4)_2 \qquad (2)$$
$$[M = Ni(II), Cu(II)]$$
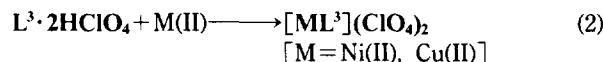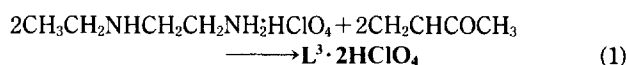
The reaction of the ligand with Cu(II) salt gives to the reddish purple complex, [CuL³](ClO₄)₂. The infrared spectra (Table 1) shows the presence of the characteristic vibrations for C=N bond at $v_{C=N}$ (1663 cm⁻¹) and perchlorate bands (1107 and 625 cm⁻¹). But no absorption of N-H vibration around 3200 cm⁻¹ is shown. The electronic spectra of this complex shows a single d-d band at $\lambda_{max} = 532$ nm with a molar extinction coefficient of 207. The position of this band and the value compare quite well with those reported by other copper(II) tetra-aza macrocyclic complexes². Also the ligand forms the yellow complex with Ni, [NiL³](ClO₄)₂. Its infrared spectrum also shows the bands expected for the characteristic vibrations of C=N bond at $v_{C=N}$ (1650 cm⁻¹) and perchlorate bands (1092 and 624 cm⁻¹) (Table 1). This complex [NiL³](ClO₄)₂ shows a strong band in aqueous solution at $\lambda_{max} = 455$ nm ($\epsilon = 134$ dm³mol⁻¹cm⁻¹) typical of singlet ground-state Ni(II)⁷. There is little tendency to add water