Notes

Radical Intermediate in the Formation of Ethyllithium from Ethyl Halide and Lithium Metal

Bong Jin Park

Department of Chemistry, Sun Moon University,
Choong Nam 337-840, Korea

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One of the most versatile reagents in organic chemistry is organolithium compounds.[1] There are two major methods to make them. One is hydrogen-metal exchange (metallation), (eq. 1) and the other is halogen-metal exchange (HME), (eq. 2).

$$RLi + R'H \rightarrow RH + R'Li \quad (1)$$

$$RLi + R'X \rightarrow RX + R'Li \quad (2)$$

However, many simple alkyl- and aryllithium compounds could be made by a procedure similar to that for the Grignard reagents. Although this direct method is easy and simple, it was not very mucyh popular[2] until proper conditions were developed. For high yields of organolithium compounds by this method, there are the most important factors to be considered.[1a] They are as follows: the nature of the halides, the purity and physical state of the lithium metal, the nature of alkyl groups and solvents. Yet the mechanism of the reaction of alkyl halides with lithium is not well understood. Several research groups[3] studied this reaction to elucidate the mechanism and showed stereochemical evidences, which suggested that radical intermediate is involved. In addition to these stereochemical studies, a kinetic study showed that the reaction is a pseudo first order, four-centered transition state.[4]

The above results let us to further study the mechanism, and this is the paper about the results obtained.

Experimental

Materials. All reagents and solvents were purified before use, unless specified. Lithium metal (1% wt. Na) in 30% mineral oil was obtained from Alfa chemicals. Ethyl iodide and ethyl bromide were purified by distillation over CaH_2 under N_2 gas dried. Di-*n*-butyl ether (DBE) was purchased from Aldrich and purified with the known procedure. A 98% pure phenyl-*N*-*t*-butylnitrone (PBN) was purchased from Aldrich and used as received.

General conditions and apparatus. All reactions were carried out under an atmosphere of argon gas, which was dried over molecular sieves (4 Å) and drierite ($CaSO_4$, blue).

A Varian E-109ES spectrometer was used to conduct the electron spin resonance study.

General procedure for reactions of alkyl halides with lithium. 0.038 g (0.22 mmol) of PBN solution in 0.30 mL in DBE and 0.30 mL (0.30 mmol) of Li in mineral oil were mixed in an ESR tube under argon gas by using syringes. 0.093 g (0.60 mmol) of EtI or 0.065 g (0.060 mmol) of EtBr were added to the mixture above under argon gas and then scanning was begun.

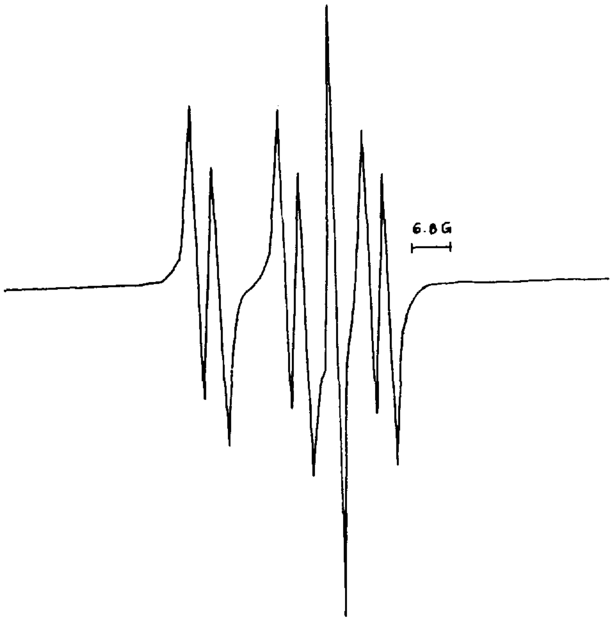


Figure 1. ESR spectrum of the PBNEt radical formed in the reaction of ethyl bromide with Li (1% wt. Na) in DBE at r.t. (scanned in 5 min. after mixing.).

Results and Discussions

Methodology used for this study is spin trapping technique,[5] which uses a spin trapping agent to form a more stable free radical from a reactive radical intermediate, if any, in the systems, and the radical trapped can be easily detectable in ESR spectrometer.

In a specially designed ESR tube, either ethyl iodide or ethyl bromide as a probe alkyl halide was allowed to react with lithium metal in the presence of the spin trapping agent, PBN (phenyl *N*-*t*-butylnitrone). ESR spectra (Figure 1, Figure 2, Figure 3) of the products (PBNR·) formed from the reactions were obtained, which are about the same as those reported from the methods of both photolysis and alkyllithium with O_2 gas by Janzen *et al.* ($A_n \approx 13.95$ gauss, $A_\beta H \approx 3.19$ gauss).[5a] And these results would indicate that a radical intermediate (R ·) is involved in the reaction. However, spectrum (Figure 3) obtained from ethyl iodide is not so sharp as the one from ethyl bromide. This could be explained by the fact that iodine atom in EtI is less electronegative and more polarizable than that of the bromine in EtBr, this might cause ethyl group to have a less free radical character in EtI to form a PBNR · during the reaction. To confirm the origin of radical formed whether by the reaction or not, let

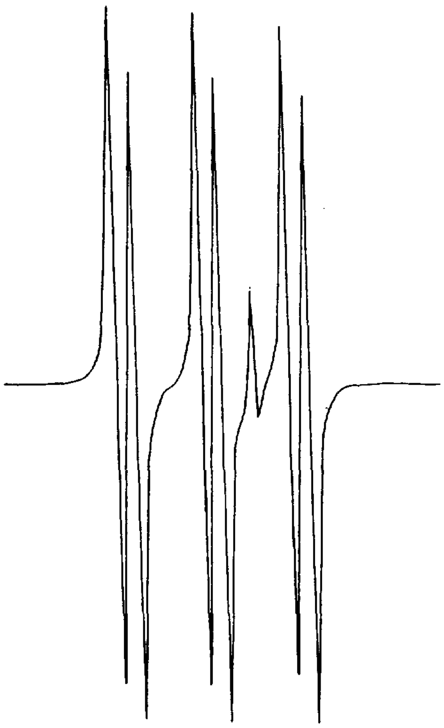


Figure 2. ESR spectrum of the same sample that in Figure 1. (scanned in 30 min. after mixing.).

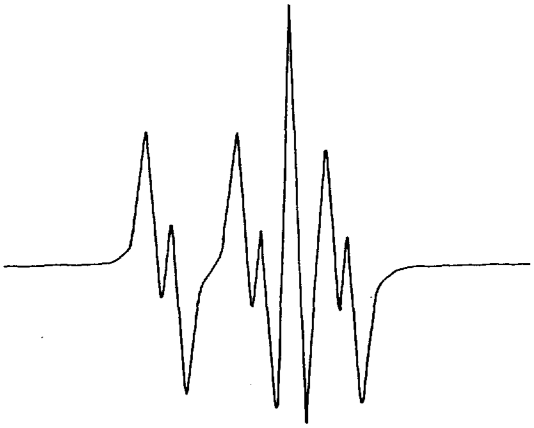
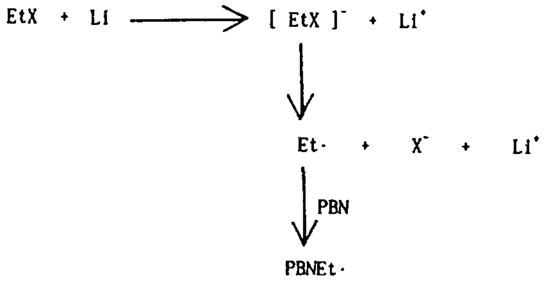


Figure 3. ESR spectrum of the PBNEt radical formed in the reaction of ethyl iodide with Li (1% wt. Na) in DBE at r.t. (scanned in 5 min. after mixing.).

the reaction, where EtBr was the reagent of choice because of its well resolved hyperfine splitting (Figure 1), go further for 30 min., then ESR spectrum was taken. The spectrum (Figure 2) obtained after 30 min. has intensities higher than the one (Figure 1) after 5 min., which indicates that the concentration of the radical (PBNEt $\cdot$) was kept increasing not by other sources including any adventitious impurities but by the reaction itself (EtX+Li). A suggested mechanism is that the first step is to transfer an electron from Li metal to ethyl halide to form a radical anion, which is then split into ethyl radical and halide anion, (Scheme 1).



Scheme 1. Scheme for the formation of PBNEt radical from the reaction of EtX (X=I, Br) with Li metal.

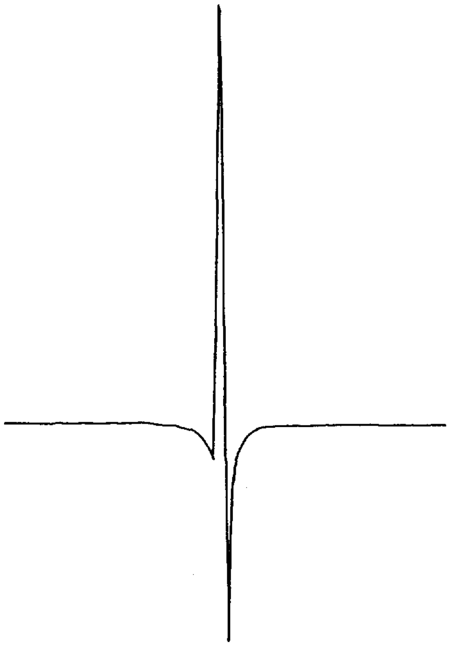


Figure 4. ESR spectrum of Li (1% wt. Na) with PBN in DBE at r.t. shows only one singlet by Li metal itself.

This result was further verified through three control experiments which might affect the spectra obtained. The first experiment was carried out in order to rule out the possibility of reaction between ethyllithium initially produced and ethyl halide left, which is known as halogen-metal exchange. Because of its radical nature,[6] this reaction might also give the same spectrum that from the title one. For the convenience or doing experiment, *n*-BuLi which is commercially available with known concentrations and *n*-BuI/or Br were used. However, when 0.30 mmol of *n*-BuLi was mixed with 0.30 mmol of *n*-BuI/or *n*-BuBr in dibutyl ether as a solvent, no signal was found. Perhaps, *n*-BuLi could have reacted with PBN to produce $PBNR^-Li^+$, which is of course, not active in ESR.[5a] In the second control experiment, lithium metal was allowed to mix with PBN, no sign of radical formed observed either (Figure 4). Finally, *n*-BuLi was mixed with PBN to check out for the possibility of a PBNR radical, yet no ESR spectrum was obtained either. On the other hand, when a dried O_2 gas was introduced to this mixture (*n*-BuLi+PBN), a well resolved hyperfine ESR spectrum with high intensity was observed, which has already been known.[5a] Therefore, the formation of ethyllithium from ethyl halides (iodide and bromide) with lithium metal is believed to occur *via* a radical intermediate at least some extent, and this observation provides the first spectroscopic evidence of a radical nature of an intermediate produced by single electron transfer (SET) pathway[7] in the reaction of an ethyl halides with lithium metal.

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Template Synthesis of Nickel(II) Complexes with Dianionic BenzoN_4 Macrocycles

Yu Chul Park*, Zun Ung Bae, Seong Su Kim,
and Sun Kee Baek

Department of Chemistry,
Kyungpook National University,
Taegu 702-701, Korea

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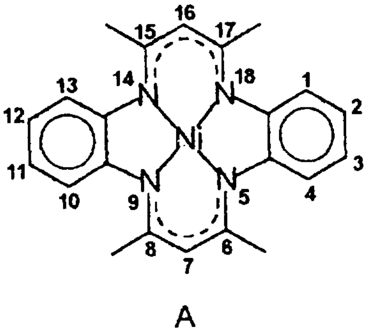
During a series of studies of tetraaza[14]annulene[1] nickel(II) complex A, the macrocyclic complex obtained by template condensation of 1,2-phenylenediamine with 2,4-pentanedione in the presence of nickel(II) ion first described by Jäger,[2] a large number of macrocyclic complexes based on the macrocyclic complex A framework were synthesized and characterized.[3~5]



A

Tetraaza[14]annulene metal complexes have a number of structural features in common with the porphyrins[6,7] and the complexes have also received much attention as catalysts, and as precursors for electrically conductive polymers.[8] However, most macrocyclic complexes[9~12] obtained by Jäger method were symmetrical macrocyclic complexes which were formed from two molecules of diamine and two molecules of β-diketone.

In this paper, we report the synthesis of the new nickel(II) complexes with dianionic benzoN_4 macrocycles, 2,4,9,11-tetramethyl-1,5,8,12-(benzo)tetraazacyclotetradecinato(2-)nickel(II) (**1a**), 2,4,10,12-tetramethyl-1,5,9,13-(benzo)tetraazacyclopentadecinato(2-)nickel(II) (**1b**), 2,4,9,11-tetramethyl-1,5,8,12-(14-nitrobenzo)tetraazacyclotetradecinato(2-)nickel(II) (**2a**) and 2,4,10,12-tetramethyl-1,5,9,13-(14-nitrobenzo)tetraazacyclopentadecinato(2-)nickel(II) (**2b**), by the template condensation of a 1 : 1 mixture of the appropriate phenylenediamine(*e.g.*, 1,2-phenylenediamine and 4-nitro-1,2-phenylenediamine) and alkyldiamine (*e.g.*, ethylenediamine and propylenediamine) with 2,4-pentanedione in the presence of nickel(II) salt. The spectroscopic properties of the nickel(II) macrocyclic complexes **1a, 1b, 2a** and **2b** shown in Figure 1 are also discussed.

Experimental

Measurement

Infrared spectra of the complexes were recorded as disks in KBr on a Perkin-Elmer 1430 IR spectrophotometer. ^1H (300 MHz) and ^{13}C (75.5 MHz) spectra were recorded with a Bruker instrument in $CDCl_3$ with TMS as an internal reference. Elemental analyses were performed by Kolon R & D center. Electronic absorption spectra were obtained on a Shimadzu UV-265 spectrophotometer.

Synthesis

All reagents and solvents used were of analytical grade.

2,4,9,11-tetramethyl-1,5,8,12-(benzo)tetraazacyclotetradecinato(2-)nickel(II) (1a). The complex was prepared by a modification of the procedure described by Jäger[2] and Cameron.[13]

2,4-Pentanedione (0.04 mol, 4 g) was added to the methanol (50 mL) solution of nickel(II) acetate tetrahydrate (0.02