teristic of cation radical species at 420 nm, however for Zn-Pc the electron transfer reaction experiment in p-benzoquinone could not be done because of the decomposition in the ground state.

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Synthesis and Characterization of New Organotin (IV)-phenylenebisdithiocarbamate Complexes

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New di- and triorganotin(IV) complexes of meta- and para-phenylenebisdithiocarbamate(m- and p-pbdtc) have been synthesized and characterized by means of chemical analysis, mass spectrometry, and IR spectroscopy. The reaction of the m-pbdtc ligand with diorganotin(IV) halides resulted in 1:1 products, $R_2Sn \cdot$m-pbdtc (R = Me, Cy, n-Bu) of dimeric nature whereas the p-pbdtc ligand led to an oligomeric or polymeric structure. The pbdtc ligands were also reacted with triorganotin(IV) halides to form monomeric complexes, $(R_3Sn)_2 \cdot$pbdtc. The tin coordination chemistry of these complexes were also discussed in terms of Sn-C and Sn-S bonding modes.

Introduction

Since the first report on phenyltin(IV) dithiocarbamates in 1965[1] dithiocarbamate complexes of alkyltin(IV) or aryltin(IV) with sulphur as the donor atom have been extensively studied with a view to establish relationship between structure and biological activity. The chemical and spectroscopic studies of these complexes have revealed that tin atom can expand its coordination number above four and that dithiocarbamate ligand would be monodentate or bidentate.[2-6] In the previous study[7] diorganotin(IV) ethylenebisdithiocarbamate (ebdtc) complexes of the type $R_2Sn(S_2CNHCH_2)_2$ were synthesized in our laboratory and characterized by X-ray crystallographic study. In an effort to extend this chemistry we wish to report the syntheses and properties of the new organotin(IV) complexes of the m- and p-phenylenebisdithiocarbamate (m- and p-pbdtc) ligands.

Experimental

All preparations were performed under a nitrogen atmosphere with the use of standard Schlenk ware techniques. Reagent grade chemicals were used without further purification. Chemical analyses were carried out by the Chemical Analysis Laboratory at KAIST. H-NMR spectra were recorded on samples in fresh DMSO-d_6 on a Varian EM-360A (60 MHz) or a Varian FT-80A Spectrometer. The infrared spectra in the 300-400cm^{-1} region were measured on KBr pellets with a Perkin-Elmer 283B Spectrophotometer and the infrared spectra in the 400-4000cm^{-1} region were measured on KBr pellets with an Analect Instrument fx 6160 FT-IR Spectrometer. The mass spectral data were obtained from a JEOL JMS-DX 303 Mass Spectrometer using a fast atom bombardment (FAB) mode. Xenon gas at 6 KV energy was used at the neutral atom beam and nitrobenzyl alcohol was used as a matrix for FAB. Scan range of m/e = 100 - 2,500, scan speed of 60 sec FS, acceleration voltage of 5.0 KV and ion multiplier voltage of - 1.4 KV were applied to obtain the mass spectrum.

Preparation of m- and p-pbdtc ligands. Na_2(p-pbdtc) ligand was prepared by the literature method.[8] The yellowish green solid thus obtained was recrystallized from a H_2O-acetone solvent pair (1:4) to produce the tetrahydrate in 79% yield. m.p. 260°C. Anal. Calc. for $C_8H_6N_2S_4Na_2 \cdot 4H_2O$: C,25.53; H,3.72; N,7.44. Found: C,24.80; H,3.31; N,7.10
H-NMR (δ, ppm): 7.7(s, -Ph-), 10.0(br, -NH-)
IR(cm^{-1}); ν(C-N), 1507(s); ν(C-S), 979(s).

The same procedure was used to prepare the disodium salt of m-pbdtc, which was recrystallized from a H_2O-EtOH solvent pair (1:4) to produce the tetrahydrate in 78% yield. m.p. 247°C. Anal. Calc. for $C_8H_6N_2S_4Na_2 \cdot 4H_2O$: C,25.53; H,3.72; N,7.44. Found: C,25.70; H,3.77; N,7.42
H-NMR (δ, ppm): 7.4(m, -Ph-), 10.2(s, -NH-)
IR(cm^{-1}): ν(C-N), 1489(s); ν(C-S), 1006(s)

Synthesis of organotin(IV)·pbdtc complexes. R_2Sn·m-pbdtc (R = Me, Cy, n-Bu): Na_2(m-pbdtc) (2 mmol) in 100m*l* of methanol was added dropwise to an equimolar solution of dimethyltin dichloride in 100m*l* of methanol. After the reaction mixture was cooled to about 0°C, the NaCl formed was filtered off. The filtrate was condensed to approximately 100m*l* with a rotary evaporator and then excess distilled water was added slowly to the filtrate to precipitate the product. The resultant off-white solid was recrystallized from a THF-petroleum ether (1:2) solvent pair. The crystalline solid (m.p. 194°C) was obtained in 76% yield. Anal. Calc. for $(CH_3)_2Sn \cdot (C_8H_6N_2S_4)$: C,2951; H,2.95; N,6.88; Sn,29.2. Found: C,29.50; H,2.78; N,6.85; Sn,28.2
H-NMR (δ, ppm): 0.8(s, -Me), 7.1(d, -Ph-), 9.8(br, -NH-)
IR(cm^{-1}): ν(C-N), 1515(s); ν(C-S), 1015(s), 1030(s); ν(Sn-C), 540(s) 510(sh); ν(Sn-S), 310(Sh), 325(s).

The dicyclohexyltin·m-pbdtc complex was obtained by the same procedure. The resultant off-white solid was recrystallized from the THF-petroleum ether (1:2) solvent pair. The crystalline solid (m.p. 198°C) was obtained in 76% yield. Anal. Calc. for $(C_6H_{11})_2Sn \cdot (C_8H_6N_2S_4)$: C,44.20; H,5.16; N,5.16; Sn,21 9. Found: C,43.20; H,5.55; N,4.86; Sn,22.5
H-NMR (δ, ppm): 1.4(m, -Cy), 7.4(m, -Ph-), 9.7(br. -NH-)
IR(cm^{-1}); ν(C-N), 1515(s); ν(C-S), 1005(s), 1030(s); ν(Sn-S), 320(s)

The di-n-butyltin·m-pbdtc complex was also obtained in white solid (m.p. 177°C) in 78% yield. Anal. Calc. for $(n\text{-}C_4H_9)_2Sn \cdot (C_8H_6N_2S_2)$: C,39.13; H,4.90; N,5.71; Sn,24.2. Found: C,39.24; H,4.82; N,5.34; Sn,23.9
H-NMR (δ, ppm); 1.0(m, -n-Bu), 7.1(d, -Ph-), 9.8(br, -NH-)
IR(cm^{-1}): ν(C-N), 1520(s); ν(C-S), 1030(s); ν(Sn-S), 360(s)

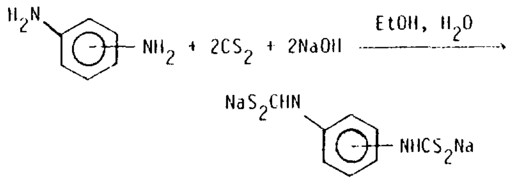
$(CH_3)_2Sn$·p-pbdtc: The dimethyltin complex of p-pbdtc ligand was prepared by the same procedure as in the m-pbdtc analog. A yellowish solid (dec. 291°C) was obtained in 76% yield. Anal. Calc. for $(CH_3)_2Sn \cdot (C_8H_6N_2S_4)$: C,29.51; H,2.95; N.6.88; Sn,29.2. Found: C.29.00; H.2.99; N,6.40; Sn,29.6
IR(cm^{-1}): ν(C-N), 1515(s), 1550(s); ν(C-S), 1010(s), 1025(sh); ν(Sn-S), 340(s), 360(sh).

$(Ph_3Sn)_2$·m-pbdtc and $(Ph_3Sn)_2$·p-pbdtc: Na_2(m-pbdtc) (2 mmol) in 100m*l* of methanol was added dropwise to the solution of triphenyltin chloride (4 mmol) in 100m*l* of methanol. After the reaction mixture was cooled to about 0°C, the NaCl formed was filtered off. The filtrate was condensed to approximately 100m*l* using a rotary evaporator and then excess distilled water was added slowly to the filtrate to precipitate the product. the white solid was recrystallized from a THF-petroleum ether (1:2) solvent pair. The white solid (m.p. 197°C) was obtained 75% yield. Anal. Calc. for $[(C_6H_5)_3Sn]_2 \cdot (C_8H_6N_2S_4)$: C,55.15; H,3.76; N,2.92; Sn,24.8. Found: C,54,88, H,3.78, N,2.90; Sn,24.9
H-NMR (δ, ppm); 7.6(d, -Ph), 7.7(br, -Ph-), 9.9(br, -NH-)
IR(cm^{-1}): ν(C-N), 1530(s); ν(C-S), 920(s); ν(Sn-S), 370(s)

The $(Ph_3Sn)_2$·p-pbdtc analog was prepared exactly by the same method employing Na_2(p-pbdtc) and obtained as a white solid in 74% yield. Anal. Calc. for $[(C_6H_5)_3Sn]_2 \cdot (C_8H_6N_2S_4)$: C,55.15; H,3.76; N,2.92; Sn,24.8. Found: C,54.59; H,3.60; N,2.88; Sn,25.8.
H-NMR (δ, ppm): 7.5(s, -Ph), 7.6(br, -Ph-), 9.7(br, -NH-)
IR(cm^{-1}): ν(C-N), 1520(s); ν(C-S), 930(s); ν(Sn-S), 370(s)

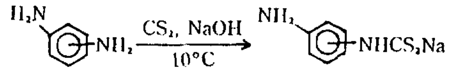
Results and Discussion

Preparation of ligands. The disodium phenylenebisdithiocarbamates were prepared from phenylenediamine, carbon disulfide and alkali metal hydroxide according to the following equation.

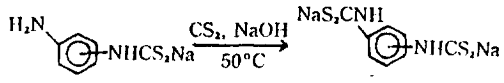


Depending on the isomeric form of the starting amine possibly can be obtained three different isomers, *para*-, *meta*- and *ortho*-pbdtc. The preparation of p-pbdtc of these isomers has been reported by van der Ker.[9] In the procedure diammonium p-pbdtc was prepared by adding aqueous ammonia to the mixture of p-phenylenediamine and carbon disulfide and then the amonium cation was exchanged with sodium ion. In the present work, however, disodium p-pbdtc could be obtained directly by adding carbon disulfide dropwise to the mixture of sodium hydroxide and p-phenylenediamine. Thus disodium p-pbdtc was obtained by the following two step reactions.

1st step:



2nd step:



The first basicity constant K_b of p-phenylenediamine is 1.4×10^{-8}, and the first step dithiocarbamation can be accomplished at relatively low temperature. However, the basicity of phenylenedithiocarbamate thus formed may be remarkably decreased and the second step reaction needed higher temperature. Therefore, the final product, pbdtc could be obtained by raising the reaction temperature to 50°C for 1 hour. The resultant yellowish green solid of disodium p-pbdtc was recrystallized from a mixture (1:4) of water and acetone. The final product was obtained as a tetrahydrate and was stable for a long time in a nitrogen atmosphere. Disodium m-pbdtc of the yellowish brown solid was also obtained as a tetrahydrate in the same way as described in the above. However, several attempts to prepare disodium *o*-pbdtc have not been successful but, instead, resulted in *o*-phenylenethiourea probably due to coupling of the two dithiocarbamate groups nearby.

Synthesis of organotin (IV)·pbdtc compleses. The equimolar reaction of R_2SnCl_2(R = Me, Cy, n-Bu) with Na_2(m-pbdtc) in ethanol afforded the products of the type R_2Sn·m-pbdtc, as established by chemical analysis and spectroscopy, probably due to the metathesis reaction represented by the following reaction.

$$R_2SnCl_2 + m\text{-}C_6H_4(NHCS_2Na)_2 \xrightarrow[RT]{EtOH}$$

$$R_2Sn\cdot m\text{-}C_6H_4(NHCS_2)_2 + 2NaCl$$

(R : Me, Cy, n-Bu)

Most bivalent transition metal ions are known to react with the ebdtc ligand to form insoluble polymeric products of the type $\leftarrow M\text{-}S_2CNHCH_2CH_2NHCS_2 \rightarrow_n$, M = Mn, Zn, Fe, etc.[10-13] Unlike such transition metal complexes, the diorganotin(IV) complexes with the ebdtc ligand were found to be dimeric both in solution and in the solid state.[7] In order to prevent possible formation of polymeric species we originally carried out the syntheses of R_2Sn·m-pbdtc in dilute solution. However, although more concentrated solutions were used, the same products were obtained. Thus the absence of polymeric materials in the R_2Sn·m-pbdtc system is intrinsic and is not the result of a particular synthetic strategy.

The similar reaction of Me_2SnCl_2 with the p-pbdtc ligand in methanol resulted in a yellowish solid of the same composition.

The reaction of disodium salts of m- and p-pbdtc with Ph_3SnX in mole ratio of 1:2 resulted in a solid product of the expected composition as shown by the result of chemical analysis, probably due to the following reaction.

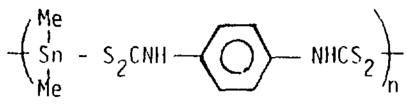
$$2R_3SnX + m\text{-}, p\text{-}C_6H_4(NHCS_2Na)_2 \xrightarrow[RT]{EtOH}$$

$$m\text{-}, p\text{-}C_6h_4(NHCS_2SnR_3)_2 + 2NaX$$

(R = Ph, Cy; X = Cl or Br)

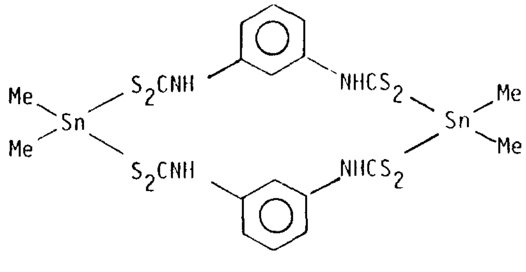
Increased mole ratio of triorganotin chloride to the pbdtc ligand led to the same product. These triorganotin(IV)·pbdtc complexes were further characterized by H-NMR and IR spectroscopies and mass spectrometry.

Structure and physical properties of organotin(IV)·pbdtc complexes. Diorganotin(IV)·pbdtc and bis-triorganotin (IV)·pbdtc complexes are soluble in polar solvents such as THF, DMSO, and less soluble in benzene, toluene, acetone and ethanol, but insoluble in water and aliphatic hydrocarbons. Dimethyltin(IV)·p-pbdtc complex, however, is insoluble in most organic solvents and decomposed at 220°C without melting point, which suggest that the p-pbdtc analog may be an oligomeric or polymeric form of the following structure.



In contrast to this, the m-pbdtc analog seems to be a dimeric form as is seen in its mass spectrum given in Figure 1. The mass spectrum was scanned up to m/e = 2,500 but no ions were detected beyond m/e = 850. The spectrum shows the molecular ion (D^+-2) of the dimer form $[Me_2\cdot Sn\cdot$m-pbdtc$]_2$ at m/e = 814. Also shown is a monomer ion Me_2Sn·m-pbdtc at m/e = 408 which may be a fragment from the dimeric parent ion. The relative mass spectral intensities of the peaks around m/e = 408 and m/e = 814 match well with theoretical ionic distribution as shown in Table 1. The complexity actually arises from a complicated isotopic pattern of tin itself also shown in the table. Such a dimeric structure has already been found by our previous X-ray crystallographic study[7] in the diorganotin(IV) complexes of the similar ebdtc ligand, in which one of the dithiocarbamate moiety acts as a bidentate and the other as a monodentate, thus the tin metal being in a trigonal bipyramidal coordination.

In the dimeric structure of the dimethyltin(IV)·m-pbdtc shown in the below, the local geometry of the tin atom depends on the nature of coordination by the dithiocarbamate groups of the m-pbdtc ligand.



It is generally known that there are two basically different bonding modes of the dithiocarbamate(dtc) moiety in its metal

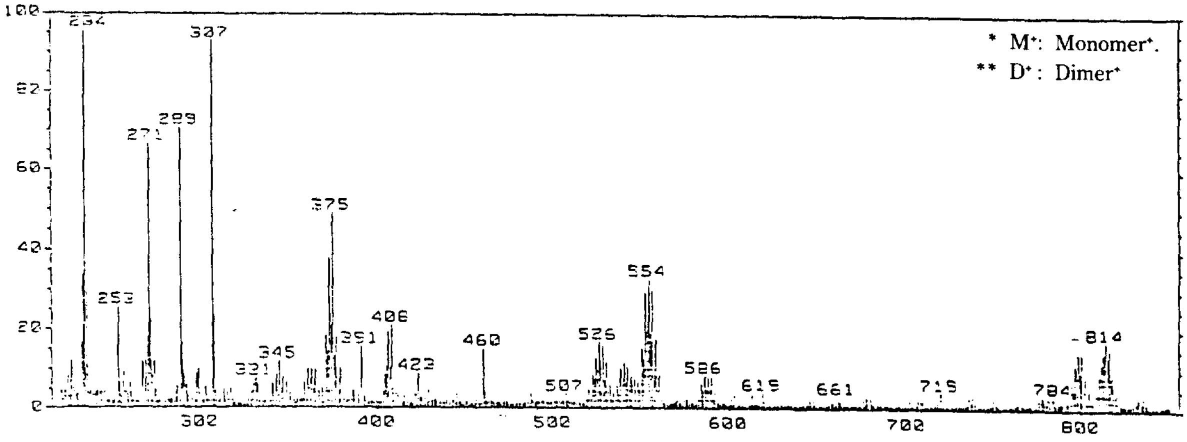
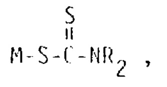


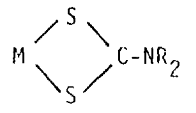
Figure 1. Mass spectrum of Me_2Sn(m-pbdtc).

Table 1. Theoretical Ion Distributions

Sn		$Me_2Sn\cdot$m-pbdtc		$(Me_2Sn\cdot$m-pbdtc$)_2$	
Mass	Ratio	Mass	Ratio	Mass	Ratio
111.9048	2.881	401.8911	1.656	809.7819	1.854
113.9028	1.971	402.8921	1.119	810.7820	10.723
114.9033	1.031	403.8901	36.717	811.7806	66.488
115.9017	43.191	404.8915	25.030	812.7818	58.095
116.9030	22.960	405.8898	70.989	813.7802	100.000
117.9016	72.824	406.8913	35.794	814.7811	62.379
118.9033	26.024	407.8901	100.000	815.7797	81.992
119.9022	100.000	408.8912	18.894	816.7805	30.950
121.9034	14.286	409.8867	17.494	817.7775	23.937
123.9053	18.138	410.8883	2.594	818.7786	6.261
		411.8839	1.516	819.7748	3.290


$M{-}S{-}\overset{\overset{S}{\|}}{C}{-}NR_2$,

(I)



(II)

complexes. In order to distinguish between the monodentate (I) and bidentate (II) structures extensive IR studies[14-18] on Sn-dtc complexes have been carried out, since the stretching modes for the C-N, C-S and Sn-S bonds are known to be sensitive to the molecular structure. In particular, Bonati and Ugo[14] proposed that the C-S stretching mode appearing in the range 950-1050 cm^{-1} can be a criterion for discerning the dtc bonding type. Thus in the further modified Bonati-Ugo method, splittings larger than 20 cm^{-1} of the ν(C-S) band were taken to indicate monodentate bonding (I) whereas those less than 20 cm^{-1} suggest bidentate bonding (II). However, in recent years it has strongly been suggested that the bands in the 950-1050 cm^{-1} region can not be used to discern the bonding type of the dtc ligand, since their splittings are due to intraligand coupling of ν_{as}(C-S) modes with the ν(R-N) modes.[19] In fact, it was very difficult to apply Banati-Ugo method to our organotin(IV)·pbdtc systems as is seen in the IR spectra of some typical complexes in Figure 2. Therefore, it seems now more reasonable to discuss the coordination chemistry of organotin compounds in terms of direct Sn-S or Sn-C bonding modes rather than C-S modes.

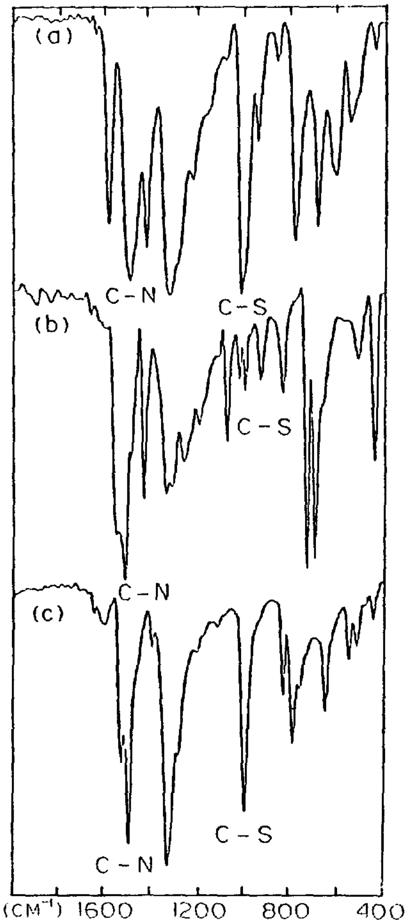


Figure 2. IR Spectra of $Me_2Sn\cdot$m-pbdtc (a), $(Ph_3Sn)_2\cdot$p-pbdtc (b), and $Me_2Sn\cdot$p-pbdtc (c).

Unfortunately, IR studies on Sn-S bonding modes of Sn-dtc complexes are rare, but there are a good deal of spectral data on Sn-C bonds.[20,21] Among other things the most useful information on the diorganotin compounds is that two ν(Sn-C) bands are observed in the 500-560 cm^{-1} region for *cis*-configuration of the organic groups while only one appears for the *trans*-configuration. The measured frequencies of ν(Sn-C) and ν(Sn-S) are given in Table 2 for the representative $Me_2Sn\cdot$pbdtc complexes along with some known similar compounds.

Table 2. IR Bands of ν(Sn–C) and ν(Sn–S) Modes

Compounds	ν(Sn–C)	ν(Sn–S)
$(t\text{-}Bu)_2Sn \cdot ebdtc$[22]	507(m), 545(m)	345(m), 390(s)
Me_2SnCl_2[20]	524(s), 563(s)	–
$Me_2Sn \cdot (dtc)_2$[22]	559(m)	367(s)
$Me_2Sn \cdot p\text{-}pbdtc$	510(s), 543(s)	340(s), 360(sh)
$Me_2Sn \cdot m\text{-}pbdtc$	510(sh), 540(s)	310(sh), 325(s)

The spectral data in the table indicate that the methyl groups in both of $Me_2Sn \cdot$pbdtc complexes are in *cis*–configuration. Furthermore, it is very interesting to compare the ν(Sn–S) modes of the pbdtc complexes with those of other known compounds in the table. For instance, $Me_2Sn(dtc)_2$[2] which is known to have an octahedral coordination with the methyl groups in trans configuration exhibits only one ν(Sn–S) band whereas two ν(Sn–S) bands are observed for the ebdtc compound in which the tin atom in a trigonal bipyramidal coordination with one chelated and one monodentate dithiocarbamate groups.

It is suggested from such spectral comparisons that the local geometry of the tin metal in the $Me_2Sn \cdot$pbdtc complexes is probably not an octahedral but trigonal bipyramidal or tetrahedral structure. For more decisive conclusion, extensive study on the IR spectra of these compounds is necessary.

The H-NMR spectra of organotin(IV)·pbdtc complexes exhibit three kinds of proton resonances: N–H proton resonance appears as a singlet at $\delta = 9.7 - 9.9$ ppm, phenyl protons as a multiplet at round $\delta = 6.5 - 7.7$ ppm and aliphatic C–H in the range of $\delta = 0.8 - 2.1$ ppm. Their integrations are consistent with the proposed compositions of the complexes, but none of the NMR data could be correlated with their structural aspects.

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Reaction of Lithium 2-Pyridyloxyalkylcuprates Having Improved Thermal Stability with Acid Chlorides and α,β-Unsaturated Ketones

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A new heterocuprate containing 2-pyridyloxy ligand, lithium 2-pyridyloxy-n-butylcuprate, has shown improved thermal stability and it reacts with acid chlorides to afford the corresponding ketones in high yields. Similarly, it can be effectively utilized in conjugate addition reactions of α,β-unsaturated ketones. Of synthetic significance is that the complete utilization of n-butyl group in lithium 2-pyridyloxy-n-butylcuprate has been observed.

Introduction

Since organocuprates are capable of effecting transformations difficult to accomplish effectively with other conventional methods, they have become very popular among synthetic organic chemists for carbon-carbon bond formation reactions