Monolithium Derivatives of Acetonitrile and Phenylacetonitrile[1]

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Abstract: The monolithium derivatives of acetonitrile and phenylacetonitrile have been prepared and isolated. $LiCH_2CN$ is tetrameric while $C_6H_5CH(Li)CN$ is dimeric in dimethyl sulfoxide. Both lithium compounds are not electron deficient; association occurs by the lithium of one molecule interacting with the cyanide of an adjacent molecule. The mercury and magnesium derivatives of these compounds are also reported.

The metalation of nitriles has been studied by several groups. Acetonitrile can be monometalated by sodiohexamethyldisilazane,[2] *n*-butyllithium,[3,4] methyllithium,[5] ethyllithium,[5] and *tert*-butyllithium.[6] Dimetalation and trimetalation[3] have also been reported as well as addition to the triple bond.[5] Gornowicz and West[6] have reported that dimetalation is complete only with *tert*-butyllithium and that trimetalation never occurs; all derivatives which have been produced may be explained by a competition between metalation and derivatization.

Kaiser and Hauser[7] have prepared the mono- and dilithium derivatives of phenylacetonitrile. The identity of these were established by derivatization. We have synthesized and isolated $LiCH_2CN$ and $C_6H_5CH(Li)CN$. We report here the infrared, nmr, and uv spectra, the molecular weight, and some chemical reactions.

Experimental Section

Materials. Acetonitrile was Eastman spectrograde and was dried by passing several times through a column packed with activated alumina. Dimethyl sulfoxide (DMSO) was an Aldrich product and was also dried by passing several times through a column packed with activated alumina. Phenylacetonitrile was used as received. *n*-Butyllithium (*n*-BuLi) was obtained as a solution in hydrocarbon solvent from Alfa Inorganic. For ir work *n*-Bu^{6}Li was synthesized from ^{6}Li and di-*n*-butylmercury (Eastman). CD_3CN was obtained from Aldrich Chemical Co. and was dried as above. ^{6}Li was from Oak Ridge National Laboratory. Diethyl ether was dried by refluxing with NaK alloy and was distilled from the alloy immediately before use. Lithium analysis was by an acidimetric titration.

Spectra. Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer. Infrared spectra were run on a Beckman IR-12 instrument. Uv spectra were run on a Cary 14R spectrophotometer. All samples for spectral analysis were prepared in an NaK alloy dried, nitrogen filled drybox and were run immediately.

Synthesis. $LiCH_2CN$ was synthesized *via* the reaction of *n*-BuLi and acetonitrile carried out in diethyl ether on the vacuum line. In a typical reaction a known amount of *n*-BuLi in hydrocarbon solvent was placed in one leg of an H tube on the vacuum line. The hydrocarbon solvent was removed under vacuum and replaced with ether. A slight excess of acetonitrile was added, and the vessel was sealed off from the vacuum line and allowed to warm to room temperature. A white solid slowly precipitated as the solution turned yellow; after several hours precipitation was complete and the product was separated by filtration. The compound was removed and stored in the drybox: yield >81%; ir (Nujol mull) 2160 (s, $C{\equiv}N$), 1190 (m), 1080 (m), 1025 (m), 1025 (m), 830 (s), 575 (m, br, ν Li–cyanide), 535 (m, br), 432 cm^{-1} (m, br, ν Li–C); ir (DMSO) 3350 (m), 3250 (m), 2200 (s), 1610 (s), 1250 (m), 900 (m), 615 (m, br), 532 (m, br), 472 (m, br), 280 cm^{-1} (m); uv$_{max}$ (solid) 234 nm; uv (DMSO) 290 nm (ϵ 8×10^3); nmr (DMSO) δ 1.15 (s). *Anal.* Calcd for LiC_2H_2N: C, 51.12; H, 4.29; N, 29.81; Li, 14.77. Found:[8] C, 50.68; H, 4.45; N, 29.54; Li, 14.76.

When hexane or octane was used as the solvent the product contained less than the required amount of lithium, possibly indicating addition as well as metalation. $LiCH_2CN$ is insoluble in hexane, octane, ether, tetrahydrofuran, and dimethoxyethane. The only solvent found was DMSO.

The reaction of CD_3CN with *n*-BuLi gave metalated product as well as substantial amount of addition to the cyano group. The infrared spectrum showed an absorption at 1590 cm^{-1} ($C{=}N$), analysis gave 9.76% Li, metalation requires 14.23% Li, addition 6.48% Li. *tert*-BuLi as the metalating agent was somewhat more successful; analysis gave 12.30% Li and the ir still contained $C{=}N$. $LiCD_2CN$ was prepared *via* the reaction of $LiN[(Si(CH_3)_3]_2$[9] with CD_3CN in ether. $LiN[Si(CH_3)_3]_2$ was synthesized from $[(CH_3)_3Si]_2NH$ and *n*-BuLi in ether; to this was added CD_3CN all under high vacuum conditions. The product was separated as above: ir (Nujol mull) 2170 (s, $C{\equiv}N$), 2140 (s), 1050 (m), 950 (m), 835 (m), 769 (m), 720 (m), 700 (m), 600 (m), 575 (m, br), 510 (m, br), 410 cm^{-1} (m, br). *Anal.* Calcd for $LiCD_2CN$: Li, 14.28. Found: Li, 13.98.

$C_6H_5CH(Li)CN$ was obtained in a similar manner from *n*-BuLi and $C_6H_5CH_2CN$ in hexane. This compound was insoluble in hexane and was isolated by filtration under vacuum conditions. The compound was soluble in a variety of ether solvents giving a yellow solution: ir (Nujol mull) 2180 (s), 1920 (w), 1820 (w), 1630 (w), 1600 (m), 1290 (s), 1180 (s), 1160 (sh), 1080 (s), 1030 (m), 960 (w), 921 (w), 855 (m), 815 (m), 760 (s), 730 (s), 700 (s), 627 (w), 575 (m), 460 cm^{-1} (s, vbr); uv (solid) 228, 263, 293, 313 nm; uv (DMSO) 257 nm (ϵ 3×10^2), 293 (3×10^2); nmr (DMSO) δ 7.4 (m, 5, C_6H_5), 4.05 (s, 1, CHCN). *Anal.* Calcd for C_8H_7NLi: Li, 5.64. Found: Li, 5.02.

Conductivity. A stock solution was prepared in the drybox, the concentration was checked by titration; the remaining solutions were prepared by dilution in the drybox. The equivalent conductance of $LiCH_2CN$ is determined in a Freas cell to be 48.6 ohm^{-1} cm^{-1} at infinite dilution. For $LiCH_2CN$ in DMSO an equilibrium constant of 6×10^{-3} is obtained, for $C_6H_5CH(Li)CN$ the equilibrium constant is 9×10^{-3}.

Electrochemistry. A 1×10^{-3} *M* solution of $LiCH_2CN$ in DMSO was prepared and the cyclic voltamogram obtained using a Beckman electroscan 30. The compound was neither oxidized or reduced. A 1×10^{-3} *M* solution of anthraquinone in DMSO was likewise scanned using $N(C_2H_5)_4Br$ as the supporting electrolyte and the trace recorded. The anthraquinone was again scanned this time in the presence of LiCl, the second reduction potential was observed to back up by 160 mV. When $LiCH_2CN$ was added to the anthraquinone the second reduction potential again backed by up 160 mV. The same result was obtained when LiCl and $LiCH_2CN$ were added to the quinone; in all cases lithium ions were produced in the solution.

Molecular Weight. The molecular weights were determined by freezing point depression in DMSO; the freezing point constant for DMSO is 3.8°/m in agreement with Ranky and Nelson.[10] Solu-

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[5] I. Pattison, K. Wade, and B. K. Wyatt, *J. Chem. Soc.*, 837 (1968).

[6] G. Gornowicz and R. West, *J. Amer. Chem. Soc.*, **93**, 1714 (1971).

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[8] CHN analysis by Alfred Bernhardt Microanalytisches Laboratorium, West Germany.

[9] B. Kimura and T. L. Brown, *J. Organometal. Chem.*, **26**, 57 (1971).

tions were prepared in the drybox by weight and checked by titration. Typical values, recorded as molality (as monomer), ΔT, molecular weight were 0.056 *m*, 0.050°, 200 g; 0.216, 0.112, 215; 0.124, 0.128, 174; 0.186, 0.167, 199; calculated for $(LiCH_2CN)_4$, 188 g.

The molecular weight of $C_6H_5CH(Li)CN$ was determined both by vapor pressure lowering (Raoult's Law) in 1,2-dimethoxyethane (DME) and by freezing point measurements in DMSO. In DME values ranging from 226 to 251 g/mol were obtained; a dimer should have a molecular weight of 246 g/mol. Freezing point measurements in DMSO gave apparent molecular weights of 250–280 g.

Derivatization Reactions. $LiCH_2CN$ was prepared in the hood from *n*-BuLi and CH_3CN in tetrahydrofuran (THF). To this was added $HgCl_2$ in THF; a white air-stable product was obtained which was insoluble in all common solvents. Due to the lack of solubility no purification was attempted: ir (Nujol mull) 2180 (s, C≡N), 1150 (w), 1020 (s), 950 (s), 772 (w), 720 (w), 450 cm^{-1} (s, Hg–C).

Derivatizations were also carried out in DMSO. To a solution of $LiCH_2CN$ in DMSO was added the stoichiometric amount of metal halide. Using $HgCl_2$ a compound identical with that above was obtained; using $MgCl_2$ a magnesium derivative resulted. This magnesium compound was soluble in DMSO from which it was precipitated by the addition of benzene or cyclohexene. The precipitate consisted of a mixture of LiCl and magnesium compound which was not separated: ir (Nujol mull) 3305 (m, N–H), 1660 (s, C=N), 1025 (s), 975 (m), 730 (m), 680 (s), 580 (m), 450 (m), 360 cm^{-1} (w).

$C_6H_5CH(Li)CN$ and $MgCl_2$ in a 2:1 ratio were allowed to react as above in THF. The product was washed thoroughly in THF and dried on the vacuum line for 24 hr; it was not possible to remove the LiCl: ir (Nujol mull) 3220 (w, N–H), 2260 (vw, C≡N), 1615 (s, C=N), 1125 (w), 1110 (w), 1060 (w), 970 (w), 725 (m), 610 (m), 450 cm^{-1} (m, br).

Results and Discussions

The molecular weight studies establish that $LiCH_2CN$ is a tetramer and $C_6H_5CH(Li)CN$ is a dimer in DMSO solution. The infrared spectra of both compounds show a cyanide absorption lower than the parent compound indicating a weakening of the cyanide linkage. $^7LiCH_2CN$ shows absorptions at 432 and 575 cm^{-1}, these move to 455 and 605 cm^{-1}, respectively, in $^6LiCH_2CN$; these modes occur at 410 and 575 cm^{-1}, respectively, in $^7LiCD_2CN$. A lithium–carbon mode is expected to show a deuterium isotope effect while a lithium–nitrogen mode should be relatively insensitive to deuterium substitution. The band at 432 cm^{-1} is therefore assigned as ν_{Li-C} while the 575-cm^{-1} band, insensitive to deuterium substitution, may be associated with the interaction of lithium with the nitrogen of an adjacent molecule in the tetramer.

The spectrum becomes much more complex in DMSO solution. Vibrations are observed associated with N–H, C=N, and C–Li. West suggested the existence of several tautomeric forms:[6] $LiCH_2CN \leftrightarrow LiCH{=}C{=}NH \leftrightarrow LiC{\equiv}CNH_2 \leftrightarrow HC{\equiv}CNLiH \leftrightarrow H_2C{=}C{=}NLi$. The ir in DMSO shows the presence of several of these tautomers.

Other investigators have examined $LiCH_2CN$ as a suspension in various solvents and have normally reported two frequencies near 2000 cm^{-1}. If the $LiCH_2CN$ prepared as above is not filtered, we obtain a yellowish compound which exhibits these two absorptions; the lower absorption is probably caused by the partial formation of a dilithium compound or by addition to the CN bond.

$C_6H_5CH(^7Li)CN$ absorbs at 575 and 460 cm^{-1}; these move to 582 and 478 cm^{-1}, respectively, in $C_6H_5CH(^6Li)CN$. The 575-cm^{-1} band, by analogy to the acetonitrile case, must be assigned to the lithium–nitrogen interaction; the 460-cm^{-1} band is therefore the Li–C stretch. In DMSO bands due to C=N and N–H are observed.

The conductance of the solution poses the question as to the nature of the ions in solution. It is known that cations can complex with quinones and that this complexing has a pronounced effect on the cyclic voltamogram of the quinone.[11] For anthraquinone in dimethylformamide using a tetraalkylammonium salt as the supporting electrolyte it has been shown that cation size is the important variable.[12] No change in cyclic voltamogram is observed for cations other than lithium. When $LiCH_2CN$ is added to anthraquinone it is observed that the second reduction potential backs up. This same shift is observed whether $LiCH_2CN$, LiCl, or LiCl + $LiCH_2CN$ is added to the quinone, apparently the same cation is found in all cases. This may be DMSO–Li^+ and $(LiCH_2CN)_4$ therefore dissociates to give Li^+ and $[Li_3(CH_2CH)_4]^-$.

Mass spectroscopic investigations of ethyllithium[13] have shown that the primary ionization process is removal of an alkyl group leaving the lithium atoms undisturbed. The ionization of $(LiCH_2CN)_4$ to produce Li^+ implies that the lithiums are not protected by alkyl groups as in an electron-deficient species and therefore indicates the $LiCH_2CN$ is a novel nonelectron-deficient organolithium compound.

Further support comes from ultraviolet spectra. A transition involving the lithium framework has been predicted for tetrameric lithium compounds. Weiss and Lucken[14] suggest that this should occur near 250 nm; Cowley and White[15] indicate that it will be between 100 and 400 nm. This transition has been observed in hexameric *n*-butyllithium near 220 nm.[16] We have obtained the ultraviolet spectrum of $LiCH_2CN$ and $C_6H_5CH(Li)CN$ in DMSO solution as well as in the solid state. $LiCH_2CN$ in the solid state shows an absorption at 234 nm, which is assigned to the weakened cyanide in agreement with the ir. In DMSO solution this absorption moves to 290 nm, which may be attributed to the ketenimine as observed in the ir. The phenyl derivative cannot be exactly assigned, it is somewhat similar to that of $LiCH_2CN$, in the solid state 228 nm probably is the weakened cyanide and the rest phenyl transitions; in DMSO one of these is ketenimine, the other phenyl. No absorption which can be attributed to the lithium framework is observed down to 200 nm.

The nmr spectrum shows the expected upfield shift. $LiCH_2CN$ gives an absorption at 1.15 ppm compared to CH_3CN at 2.00 ppm, both in DMSO. In $C_6H_5CH(Li)CN$ the phenyl absorption occurs at 7.4 ppm, the benzylic proton at 4.05 ppm. No other absorptions are observed indicating that either all tautomers absorb

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at the same position or that one tautomer is present in much higher concentration than the others.

Derivatization reactions have been carried out by several authors,[2,3,6] using a variety of organic reactants. They found reaction only with the nitrile tautomer. We have carried out reactions of $LiCH_2CN$ with $MgCl_2$ and $HgCl_2$ and of $C_6H_5CH(Li)CN$ with $MgCl_2$. The infrared spectra of the magnesium compounds show absorptions near 1650 cm^{-1} (C=N) and 3300 cm^{-1} (N–H) with no absorption in the C≡N region. The mercury compound on the other hand shows a strong absorption at 2180 cm^{-1} (C≡N) and only very weak absorptions at 1632 and 3200 cm^{-1}. Magnesium chloride either preferentially reacts with one of the tautomers or rearranges to give a species with a C=N fragment; mercuric chloride, on the other hand, gives only the nitrile form.

The lithium derivatives of acetonitrile and phenylacetonitrile represent a unique class of organolithium compounds which do not have the typical electron-deficient framework. The general bonding scheme for $LiCH_2CN$ is one of intermolecular association with the lithium of one molecule interacting with the cyanide of an adjacent molecule. The lithium derivative of phenylacetonitrile is dimeric with the lithium of one molecule interacting with the cyanide of the other molecule. Studies of other nonelectron-deficient lithium compounds are currently underway.

Oxygen-18 Tracer Studies with the *trans*-Dioxobis(ethylenediamine)rhenium(V) Ion ($[Re(en)_2O_2]^+$)

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Abstract: The rate of exchange of oxygen atoms between the *trans*-dioxobis(ethylenediamine)rhenium(V) ion and solvent water has been determined. The effect of changing the $[H^+]$, [ethylenediamine], ionic strength, temperature, supporting electrolyte, solvent, and the presence of other acids and bases on the rate has been investigated. The exchange has been studied over the $[H^+]$ concentration range from 4.17×10^{-5} *M* to 6.03×10^{-13} *M*. At pH 7.00, the concentration of total uncoordinated ethylenediamine present was varied from 0.0 to 0.4397 *M*. At 50.0° and $\mu = 1.50$ (KCl), the rate law is given by $R/[Re(en)_2O_2^+] = k_0 + k_{enh_2}[enH_2^{2+}] + k_{en}[en] + k_{oh}[OH^-]$. Values for k_0, k_{enh_2}, k_{en}, and k_{oh} at this temperature were found to be $7.86 \pm 1.52 \times 10^{-5}$ sec^{-1}, $6.47 \pm 0.37 \times 10^{-3}$ M^{-1} sec^{-1}, $1.42 \pm 0.10 \times 10^{-3}$ M^{-1} sec^{-1}, and $3.26 \pm 0.31 \times 10^{-1}$ M^{-1} sec^{-1}, respectively. The Arrhenius activation energies are 30.4 ± 2.7, 30.5 ± 0.4, 18.1 ± 3.5, and 24.2 ± 2.0 kcal/mol, respectively. The rate of oxygen exchange was found to be dependent upon the nature of the positive ion of the supporting electrolyte and appears to be general acid–base catalyzed. Partial substitution of methanol for water as the solvent increased the rate. When the *trans*-$[Re(en)_2O_2]^+$ ion is oxidized, a general feature is that the trans O=Re=O group of the rhenium(V) complex is transferred essentially intact to the product ReO_4^- ion. With ClO^- ion as the oxidant, 1.908 ± 0.043 of the oxygen atoms in ReO_4^- came from the rhenium(V) complex and 2.158 ± 0.024 came from solvent water. With MnO_4^- as the oxidizing agent, 1.706 ± 0.032 oxygen atoms were transferred. When O_3 was used to oxidize the complex, 1.953 ± 0.009 oxygen atoms were transferred to ReO_4^- and 1.620 ± 0.006 of the oxygen atoms came from the solvent water.

In order to perform oxygen-transfer experiments on the oxidation of $[Re(en)_2O_2]^+$ to ReO_4^-, it was necessary to know the rate equation for exchange of oxygen atoms between $[Re(en)_2O_2]^+$ and water. The rate law for the oxygen exchange between ReO_4^- and solvent water has been reported.[2] This paper reports the rate law for the exchange of oxygen atoms between $[Re(en)_2O_2]^+$ and solvent water and its dependence upon solvent composition and temperature. The results of oxygen-18 transfer experiments are reported for the oxidation of $[Re(en)_2O_2]^+$ to ReO_4^- using several oxidizing agents.

Experimental Section

The water used in these experiments was deionized on a double-bed column, distilled from acidic $K_2Cr_2O_7$ solution and from alkaline $KMnO_4$ in an all-glass apparatus.

Reagent grade ethylenediamine was purified by slow distillation at atmospheric pressure. The first and last thirds of the distillate were discarded and only the middle fraction boiling at 116.5–117.0° (uncorrected) was used.

The concentration of solutions of ethylenediamine was determined by pH titration with hydrochloric acid standardized ultimately against standard ACS potassium hydrogen phthalate.

Perrhenic acid obtained from S. W. Shattuck Chemical Co. was used without further purification.

Oxygen-18 water was obtained from YEDA, Rehovoth, Israel, and had an ^{18}O content of approximately 1.5 atom %.

Solutions of chromium(II) perchlorate were used to remove traces of oxygen from prepurified tank nitrogen and were prepared by dissolving chromium metal in 2.0–6.0 *M* perchloric acid. Mossy

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