α Addition and Ortho Metalation of Phenyl Isocyanide[1]

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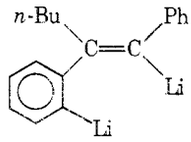
Received August 1, 1977

The reaction of *tert*-butyllithium with phenyl isocyanide in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) resulted in a product of α addition plus ortho lithiation. The ortho-lithiated lithium aldimine (**2**) formed in this manner was reacted with methyl iodide, methylene halides, carbon dioxide, phosgene, oxygen, and cuprous chloride. In addition, several novel heterocyclic compounds, 3-metalloindolines (metal = S, P, Si, Ge, and Sn), were synthesized by reacting **2** with the corresponding metallo dihalides. The new heterocyclic compounds were characterized using ^1H and ^{13}C NMR techniques.

The α addition of organolithium reagents and Grignard reagents to isocyanides has recently been reported.[2,3] The resulting metalloaldimines, which can be viewed as masked acyl carbanions, were used for the syntheses of a variety of functional groups including aldehydes-*1-d*, ketones, α-keto acids and β-hydroxy ketones.

It was observed by Mulvaney and co-workers[4] that diphenylacetylene reacted with 2 equiv of *n*-butyllithium to give as a major product **1**, which results from the trans addition to



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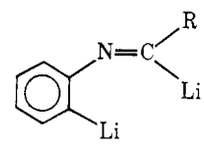

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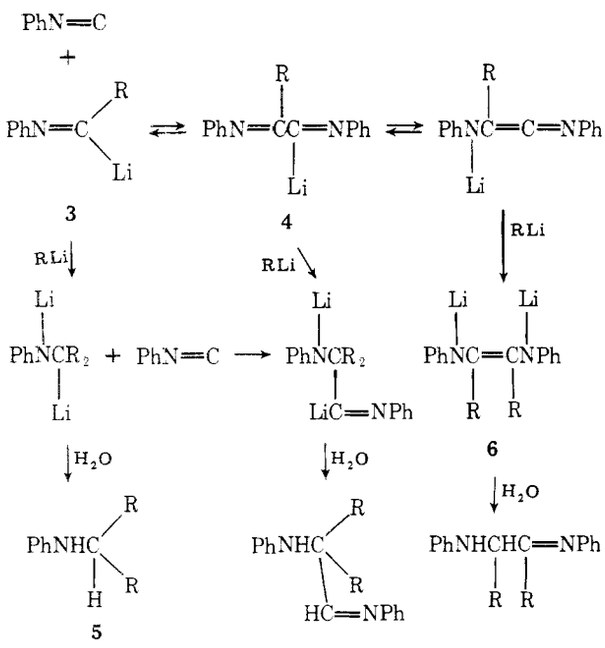
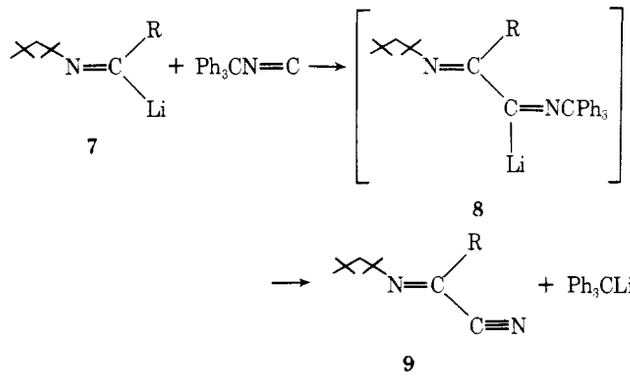
the triple bond as well as ortho lithiation. It was also shown that the ortho lithiation step could be catalyzed by the use of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA).[5,6] By analogy with this reaction, it was suggested[7] that an alkyllithium reagent and phenyl isocyanide, in the presence of TMEDA, should react to yield a product of α addition and ortho lithiation **2**.

n-Butyllithium and phenyllithium reacted with phenyl isocyanide to give products other than simple addition products.[8] *sec*-Butyllithium gave low yields (~10%) of the dilithiated aldimine **2**. It was only when *tert*-butyllithium was used that a high yield of **2** was obtained and then only if the reaction was run at −78 °C and the phenyl isocyanide was added to 2 equiv of *tert*-butyllithium. Low yields resulted if both these requirements were not met.

Scheme I. Formation and Reactions of Lithium Aldimine Dimer[8]

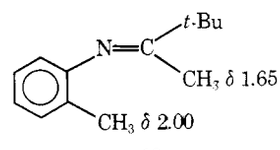


A reasonable explanation for the requirement of low temperature and the need for excess *tert*-butyllithium in solution is that the lithium aldimine **3** can further react with any excess phenyl isocyanide in solution to form a dimer[8] **4** which may then react, in a number of ways, as shown in Scheme I. This reaction scheme accounts for the formation of the secondary amine **5**, observed in the reaction of *n*-butyllithium with phenyl isocyanide.[8] An intermediate similar to **6** has also been proposed.[8] A bulky *tert*-butyl group should shift the equilibrium toward the monomeric aldimine **3** and thereby prevent unwanted side reactions. Additional support for this interpretation is provided by some recent results in our laboratory.[9] When R is *n*-butyl, the isocyanide–metal exchange reaction[10] proceeds to give a 25% yield of α-iminocyanide **9**. The lithium *tert*-butylaldimine **7** gives only trace amounts of **9** because the steric bulk of the *tert*-butyl group prevents formation of the intermediate dimer **8**.



7 **8** **9**

TMEDA is necessary for the ring-metalation step in the formation of the dilithium aldimine **2**; without it no detectable ring metalation took place after stirring for 4 h at room temperature. When the reaction mixture of lithium *tert*-butylaldimine (**3**), *tert*-butyllithium, and TMEDA was alkylated, after stirring for 1 h at room temperature with methyl iodide, a comparison (^1H NMR) of the integrated benzylic and methyl ketimine protons (**10**) showed that 65% ring metalation



10

had taken place. A 4-h time period assured >90% ring metalation. That ring metalation was, in fact, taking place at the ortho position was demonstrated by hydrolysis of **10** to yield

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Table I. C-13 Chemical Shifts[a] and ^1H NMR of the *tert*-Butyl Group for Heterocyclic Compounds

M	Registry no.	C-1	C-2	C-3	*t*-Bu
Acyclic (13)	13114-20-0	152.2	176.9	40.2	1.20
S	17626-88-9	153.4	181.5	38.3	1.49
PhP	64414-15-9	158.5	198.8	40.0	1.22
Ph_2Si	64414-14-8	161.0	200.6	40.2	1.16
Me_2Si	64414-18-2	159.6	201.7	39.7	1.24
Me_2Ge	64414-17-1	161.5	201.3	40.5	1.23
Me_2Sn	64414-16-0	159.6	*b*	4.17	1.18

[a] Ppm from Me_4Si. [b] Decomposed before least intense peak (C-2) could be recorded.

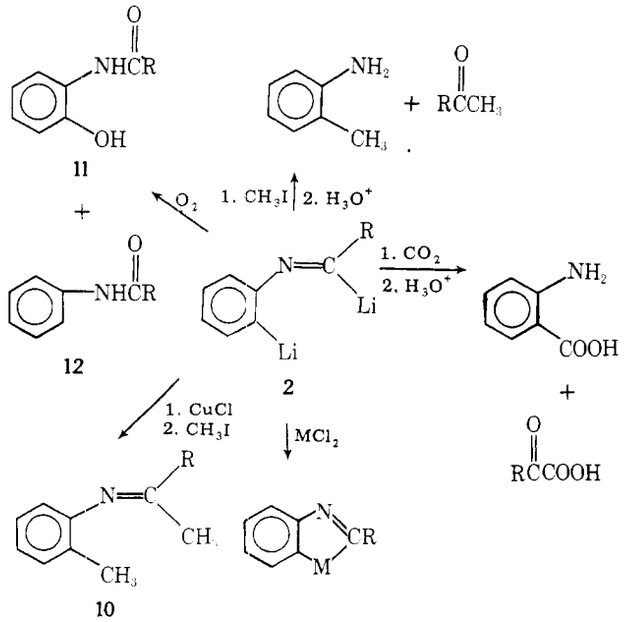
o-toluidine and methyl *tert*-butyl ketone as the sole products.[11] Moreover, treatment of the dilithium aldimine **2** (R = *t*-Bu) with carbon dioxide followed by hydrolysis yielded anthranilic acid and 2-oxo-3,3-dimethylbutanoic acid.

Attempts to synthesize 3-oxoindolines by reaction of **2** with phosgene or ethyl chloroformates or to prepare 3*H*-indoles using methylene halides proved unsuccessful. Molecular oxygen reacted with **2** to yield a mixture consisting of the *tert*-butylcarboxamides of *o*-hydroxyaniline **11** and aniline **12**, respectively. The latter amide **12** did not arise from incomplete reaction of **2**, since workup of the reaction mixture with deuterium oxide showed no deuterium incorporation. Organolithium reagents are known to react with oxidizing reagents to form radical intermediates which can then abstract hydrogen atoms from the solvent.[12]

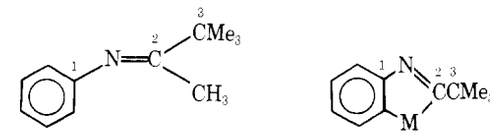
The dilithiated aldimine **2** was reacted with 1 equiv of cuprous chloride to form a lithium cuprate which when treated with methylene iodide did not yield the expected 3*H*-indole or indole itself. Reaction with methyl iodide produced the dimethylated product **10** in 65–75% yield.

The preparation of five-membered unsaturated organometallic heterocyclic and spirocyclic compounds by means of reaction between a 1,4-dilithium derivative and a metallic dihalide has been described previously. A host of metallocyclopentadienes have been synthesized starting with 1,4-dilithio-1,2,3,4-tetraphenylbutadiene.[13] Several metalloindenyl compounds of iron,[14] aluminum,[15] and selenium[16] have been prepared as well as compounds of phosphorous, silicon, germanium and tin.[6] These same workers[6] prepared spirocyclic compounds containing tin, germanium, and silicon.

Scheme II. Reactions of Dilithium Aldimine 2 (R = *t*-Bu)



Dilithium aldimine **2** was reacted with a variety of metallodihalides to generate novel heterocyclic systems (Scheme II). The new compounds were characterized using IR, ^1H NMR, UV, ^{13}C NMR and high-resolution mass spectrometry (see Experimental Section). Table I shows the ^{13}C NMR chemical shifts for the three carbon atoms in these ring systems whose chemical-shift values should be most sensitive to the effects of aromaticity. For comparative purposes, the model acyclic compound **13** is also included.



13

It should be noted that all of the heterocyclic compounds with the exception of the benzothiazole (M = S) have similar chemical shifts at carbons 1, 2, and 3. This difference between the sulfur compound and the other heterocyclic systems could be explained in terms of the heteroaromaticity of the benzothiazole and nonaromaticity of the other compounds. This argument is weakened somewhat by the observation that the chemical shifts for the acyclic model **13** more closely parallel those of the benzothiazole than they do the others. Table I shows the ^1H NMR chemical-shift values for the *tert*-butyl group. These data are more directly related to the question of aromaticity of the heterocyclic systems. It is noted that all of the compounds with the exception of benzothiazole have *tert*-butyl groups with δ values of ~1.20 ppm. The downfield chemical shift of the *tert*-butyl group of the benzothiazole relative to the other heterocyclic compounds can best be explained if the benzothiazole is the only compound which is aromatic and therefore possesses a ring current which causes deshielding (anisotropic) of the *tert*-butyl group. Therefore, of these heterocyclic 3-metalloindolines, only the benzothiazole appears to be aromatic.[14]

From a synthetic point of view it should be pointed out that the isonitrile moiety provides a means of protecting an aromatic primary amino group in order to obtain ortho metalation.

Experimental Section

Melting points were measured with a Mel-Temp apparatus. No corrections were made for either melting or boiling points. Proton nuclear magnetic resonance spectra were recorded on a Varian A-60 or Brucker 90-MHz spectrometer; chemical shifts were reported in parts per million downfield from tetramethylsilane and coupling constants are in hertz. C-13 nuclear magnetic resonance spectra were obtained using either the Brucker 90- or 270-MHz spectrometer. The chemical shifts were reported in parts per million downfield from tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 257 spectrophotometer. UV spectra were obtained with a Cary 14 spectrophotometer using 1-cm cells and concentrations of 1×10^{-4} M. Low-resolution mass spectra were recorded either on a Nuclide electron-impact mass spectrometer or a AEI-MS902 chemical-ionization mass spectrometer using isobutane as the carrier gas. High-resolution mass spectra were done on the AEI-MS902 electron-impact instrument.

Reagents. Organolithium reagents were purchased from Foote Mineral Co. and were titrated prior to use employing the method of Epplex and Dixon.[15] Mallinckrodt anhydrous ethyl ether was used directly in the preparation of phenyl isocyanide. For reactions involving organolithium reagents, the ethyl ether was distilled over lithium aluminum hydride and stored over sodium hydride prior to use. Phenyl isocyanide was distilled and stored in the freezer before using. Generally, it would last about 4 days at −40 °C before deteriorating to an unacceptable level. If there was doubt as to the quality of the phenyl isocyanide, a control reaction was run simultaneously by quenching the dilithium aldimine (**2**) with methyl iodide (see Determination of Ortho Substitution in the Experimental Section).

All other reagents were distilled or recrystallized whenever their purity was in question.

Phenyl Isocyanide. To a stirred solution of 60 g (.496 mol) of formanilide in 400 mL of dry ether with 125 g (1.24 mol) of dry triethylamine under a nitrogen atmosphere was added 71 g (0.597 mol) of thionyl chloride dropwise at such a rate that the temperature did not exceed −55 °C. After the addition was completed, the temperature was allowed to rise to −25 °C and 250 mL of saturated sodium carbonate solution was added quickly with continued stirring. The two-phase system was transferred to a separatory funnel, and the organic phase was separated, dried over anhydrous sodium carbonate, and evaporated. The residue remaining was distilled under reduced pressure to yield 23.5 g (0.228 mol, 46%) of a light yellow oil: bp 53 °C (12 mm) (lit.[15] 55 °C (15 mm)); IR (CCl_4) 2130 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.37 (s).

***N*-(1-Lithium-2,2-dimethylpropylidene)-2-lithiobenzenamine (2).** To 21.6 mmol of *tert*-butyllithium in 50 mL of anhydrous ether at −78 °C and under a nitrogen atmosphere was added dropwise over 10 min a solution of 1.0 g (9.7 mmol) of phenyl isocyanide in 15 mL of anhydrous ether. The solution was allowed to warm to room temperature, 2.5 g (22 mmol) of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was quickly added, and the solution was stirred for 4 to 12 h at ambient temperature.

***N*-(1,2,2-Trimethylpropylidene)-2-methylbenzenamine (10).** To 9.7 mmol of the dilithium aldimine (**2**) prepared as above, in 50 mL of anhydrous ether, cooled to 0 °C, was added 5.7 g (40 mmol) of methyl iodide. The solution was stirred for 30 min at ambient temperature and was then transferred to a separatory funnel, washed three times with water, and dried over anhydrous sodium sulfate. The solvent was evaporated and the residue was distilled at reduced pressure to yield 1.68 g (8.9 mmol, 92%) of **10** as a liquid: bp 73–75 °C (1.2 mm); IR (CCl_4) 1655 (s), 1600 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.07 (s, 9 H), 1.65 (s, 3 H), 2.00 (s, 3 H), 6.3–7.3 (m, 4 H); measured mass 189.1507 (rel intensity 12.8%), calcd mass 189.1517 (dev 0.9 mass unit).

Determination of Ortho Substitution. Identification of *o*-Toluidine and Methyl *tert*-Butyl Ketone. *N*-(1,2,2-Trimethylpropylidene)-2-methylbenzenamine (1.7 g, 8.9 mmol) was refluxed for 10 min in 5% aqueous hydrochloric acid and then extracted with ether. The ether solution was dried over anhydrous sodium sulfate and evaporated to yield 0.52 g (5.2 mmol/56%) of a clear liquid which was identified as methyl *tert*-butyl ketone by its IR, ^1H NMR, and the preparation of its oxime: mp 73 °C (lit.[17] 74–75 °C); IR (CCl_4) 1715 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.12 (s, 9 H), 2.08 (s, 3 H).

The acidic portion was neutralized with 10% sodium hydroxide solution, extracted with ether, dried over anhydrous sodium sulfate, and evaporated to yield 0.54 g (5.1 mmol/57%) of a liquid which was identified as *o*-toluidine by a comparison of its IR, ^1H NMR, and GLC retention times with an authentic sample of *o*-toluidine. In addition, GLC (10 ft. Carbowax 20 M, 210 °C) showed no meta or para isomers but a small amount of aniline (<5%).

Carbonation of the Dilithium Aldimine (2). Identification of 2-Oxo-3,3-dimethylbutanoic Acid and *o*-Anthranilic Acid. A solution of 9.7 mmol of dilithium aldimine (**2**) in 50 mL of ether was cooled to −78 °C and carbon dioxide was bubbled through rapidly. The solution was allowed to warm to ambient temperature with continued passage of carbon dioxide. The solvent was evaporated, 5% aqueous hydrochloric acid was added to the residue, and the mixture was refluxed 10 min, cooled, and extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate and evaporated to yield 0.917 g of a liquid which was shown to be 90% one component by GLC (6 ft Carbowax 20 M, 140 °C). The minor component was identified as 2,2-dimethylpropanoic acid by comparing retention times with an independently prepared sample from *tert*-butyllithium and carbon dioxide. The residue was recrystallized from ethyl ether–pentane to yield 0.822 g (6.32 mmol, 65%) of a solid, mp 79–81 °C, identified as 2-oxo-3,3-dimethylbutanoic acid (lit.[17b] mp 82 °C): IR (CCl_4) 3380 (m), 2960 (s), 2680 (w), 1770 (m), 1710 (s) cm^{-1}; ^1H NMR δ 1.30 (s, 9 H), 9.15 (s, 1 H).

The remaining aqueous portion was neutralized to pH 5 with 10% sodium hydroxide, extracted with methylene chloride, dried over anhydrous magnesium sulfate, and evaporated to yield a solid which was recrystallized from methylene chloride/pentane to yield 0.718 g (5.25 mmol, 54%) of a solid which did not depress the melting point of an authentic sample of anthranilic acid: IR ($CHCl_3$) 3485 (s), 3365 (s), 3200–2450 (s), 1670 (s), 1615 (s), 1590 (m), 1560 (m) cm^{-1}; ^1H NMR (CH_3CN), δ 6.0 (br, 3 H), 6.5–8.0 (m, 4 H).

Oxygenation of the Dilithium Aldimine. Identification of *N*-Phenyl-2,2-dimethylpropanamide (12) and *N*-(*o*-Hydroxyphenyl)-2,2-dimethylpropanamide (11). Oxygen was bubbled through a solution of 9.7 mmol of dilithum aldimine (**2**) in anhydrous ether cooled to −78 °C as the solution was allowed to come to room temperature. The ethereal solution was washed several times with water, dried over anhydrous magnesium sulfate, and evaporated. The residue was taken up in a minimum amount of methylene chloride, placed on a neutral alumina column, and eluted with dry ethyl ether. The first material to be eluted was 0.61 g (3.45 mmol, 36%) of a yellow solid identified as *N*-phenyl-2,2-dimethylpropanamide (**12**) by its melting point, which was 129–131 °C (lit.[17c] mp 132 °C); IR (CCl_4) 3435 (m), 1690 (s), 1600 (m) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.31 (s, 9 H) 6.8–7.7 (m, 5 H); positive chemical ionization mass spectrum P + 1 = 178.

The second, more polar fraction weighed 0.595 g (2.77 mmol, 29%) and was identified as *N*-(*o*-hydroxyphenyl)-2,2-dimethylpropanamide (**11**) by its melting point, which was 132–133 °C (lit.[17d] 133 °C): IR ($CHCl_3$) 3420 (s), 1650 (s), 1600 (m) cm^{-1}; ^1H NMR (acetone-d_6) δ 1.34 (s, 9 H), 3.33 (br, 1 H), 6.7–7.9 (m, 4 H), 8.6 (br, 1 H); positive chemical ionization mass spectrum, P + 1 = 194.

***N*-(1-Copper-2,2-dimethylpropylidene)benzenamine.** To 10.2 mmol of *tert*-butyllithium in 50 mL of anhydrous ether, cooled to −78 °C and under a nitrogen atmosphere, was added 1.0 g (9.7 mmol) of phenyl isocyanide in 15 mL of anhydrous ether over a 10-min period. The solution was allowed to come to room temperature and 0.96 g (9.7 mmol) of anhydrous cuprous chloride was added, causing an instantaneous color change. The solution of *N*-(1-copper-2,2-dimethylpropylidene)benzenamine was stirred for 2 h at room temperature.

Nitrogen was blown through the reaction vessel containing 9.7 mmol of copper aldimine solution from above, evaporating most of the ether, which was replaced with 50 mL of anhydrous THF. This solution was refluxed for 1 h, extracted with dilute ammonium hydroxide followed by saturated sodium chloride solution, dried over anhydrous magnesium sulfate, filtered through celite, and redried over anhydrous sodium sulfate. The volume of the solution was carefully reduced to 3 mL in a distilling apparatus to avoid loss of any *tert*-butyl cyanide should it be present. GLC on a 3-ft Porapak N column showed no *tert*-butyl cyanide or benzene. Preparative GLC on a 9-ft XE-60 column at 200 °C showed the previously identified *N*-phenyl-2,2-dimethylpropanamide (**12**) in 34% yield and *N*-(2,2-dimethylpropylidene)benzenamine[17d] in 30% yield: IR (CCl_4) 3050 (w), 2960 (s), 1655 (s), 1600 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.13 (s, 9 H), 6.7–7.4 (m, 5 H), 7.61 (s, 1 H); positive chemical ionization mass spectra P + 1 = 162.

Lithium Cuprate Aldimine. To 9.7 mmol of the dilithium aldimine (**2**) in ethereal solution at ambient temperature was added 0.96 g (9.7 mmol) of anydrous cuprous chloride. The dark-green solution was stirred for 1 h at room temperature.

A solution of 9.7 mmol of lithium cuprate aldimine from the above reaction was transferred to a separatory funnel and extracted twice with water and once with dilute ammonium hydroxide. The ethereal solution was filtered through celite, dried over anhydrous potassium carbonate, and evaporated to yield an oil which was crystallized in pentane to yield 9.48 g (2.7 mmol, 28%) of a solid previously identified as *N*-phenyl-2,2-dimethylpropanamide (**12**) by mp, IR, and ^1H NMR. The mother liquors were evaporated to yield 1.76 g of an oil which was analyzed by GLC (XE-60). The major component (35%) was identified as *N*-(2,2-dimethylpropylidene)benzenamine for an adjusted yield of 26%.

Methylation of the Lithium Cuprate Aldimine. To 9.7 mmol of the lithium cuprate aldimine in ether at ice-bath temperature, under a nitrogen atmosphere, was added an excess of methyl iodide (5.7 g, 40 mmol). The solution was stirred at ambient temperature for 30 min and the usual workup was carried out. ^1H NMR and GLC showed a 65–75% yield of *N*-(1,2,2-trimethylpropylidene)-2-methylbenzenamine (**10**) which has previously been identified.

***N*-(1,2,2-Trimethylpropylidene)benzenamine (13).** To 20 mmol of *tert*-butyllithium in 50 mL of anhydrous ether, at −78 °C under nitrogen, was added dropwise over a 10-min period a solution of 2.00 g (19.4 mmol) of phenyl isocyanide in 15 mL of anhydrous ether. The solution was allowed to come to 0 °C, 2.84 g (20 mmol) of methyl iodide was added quickly, and the solution was stirred for 30 min at ambient temperature. The reaction mixture was washed with water, dried over sodium sulfate, and evaporated. The residue was distilled to yield 2.95 g (15.9 mmol, 87%) of **13**: a liquid; bp 41 °C (0.01 mm); IR (CCl_4) 3050 (w), 2940 (s), 1650 (s), 1590 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.20 (s, 9 H), 1.71 (s, 3 H), 6.4–7.4 (m, 5 H); UV (CCl_4) 258 (ε 2700), 277 (ε 2700) nm; ^{13}C NMR ($CDCl_3$) δ 15.0, 27.8, 40.2, 118.9, 122.5, 128.8, 152.2, 176.9; measured mass 175.1365 (rel intensity 9.2%), calcd mass 175.1360 (dev 0.4 mmass unit).

General Procedure for the Preparation of the Heterocyclic Compounds. To 19.4 mmol of the dilithium aldimine (**2**) in 100 mL

of ether, at ice-bath temperature, was quickly added 19.4 mmol of dichloride (2.00 g of SCl_2, 3.47 g of $PhPCl_2$, 4.91 g of $(Ph)_2SiCl_2$, 2.51 g of Me_2SiCl_2, 3.38 g of Me_2GeCl_2, and 4.28 g of Me_2SnCl_2). The reaction mixture was allowed to stir at room temperature from 4 to 12 h before washing three times with water. The ethereal solution was dried over anhydrous sodium sulfate and evaporated, and the residue was distilled at reduced pressure, except in the case of the diphenyl silyl compound which was recrystallized from diethyl ether.

Characterization of 2-*tert*-Butylbenzothiazole.[18] A yellow liquid, 2.40 g (12.6 mmol, 65%), was isolated: bp 59 °C (0.01 mm); IR (CCl_4) 3050 (w), 2960 (s), 1510 (w), 1455 (w), 1440 (m), 1365 (m), 1235 (m) cm^{-1}; ^1H NMR (CCl_4) δ 1.49 (s, 9 H), 7.0–8.0 (m, 4 H); UV (CCl_4) 258 (ϵ 10 000), 284 (ϵ 1700), 295 (ϵ 1700) nm; ^{13}C NMR ($CDCl_3$) δ 30.7, 38.3, 121.3, 122.7, 124.4, 125.7, 135.0, 153.4, 181.5; measured mass 191.9746 (rel. intensity 51.2%), calcd mass 191.9768 (dev 2.3 mmass units).

Characterization of 2-*tert*-Butyl-3-phenylbenzoazaphosphole. A yellow liquid, 2.40 g (12.6 mmol, 52%), was isolated: bp 115–117 °C (0.04 mm); IR (CCl_4) 3050 (w), 2960 (s), 1480 (m), 1445 (s), 860 (s) cm^{-1}; ^1H NMR (CCl_4) δ 1.22 (s, 9 H), 7.0–8.0 (m, 9 H); UV (CCl_4) 258 (ϵ 9000) 305 (ϵ 2400) nm; ^{13}C NMR ($CDCl_3$) 30.4 (d, J = 5.6 Hz), 40.0 (d, J = 18.5 Hz), 123.4, 125.9, 128.3 (d, J = 20.3 Hz), 128.7 (d, J = 9.2 Hz), 129.2, 129.9, 131.5 (d, J = 16.7 Hz), 134.4, 134.7, 137.6 (d, J = 10.3 Hz), 158.5 (d, J = 11.1 Hz), 198.8; measured mass 267.1153 (rel intensity 100.0%), calcd mass 267.1176 (dev 2.3 mmass units).

Characterization of 2-*tert*-Butyl-3,3-diphenylbenzoazasilole. Dry ether was added to the residue and the crystals were filtered, recrystallized from ether/pentane, and placed under high vacuum (0.005 mm) at 80 °C to remove all the ether to yield 2.08 g (6.11 mmol, 63% yield) of a white solid: mp 128–129 °C; IR ($CHCl_3$) 3050 (w), 2950 (s), 1950 (w), 1885 (w), 1815 (2), 1765 (w), 1590 (s), 1115 (s) cm^{-1}; ^1H NMR δ 1.16 (s, 9 H), 7.15–7.75 (m, 14 H); UV (CCl_4) 252 (ϵ 8400), 256 (ϵ 8400), 307 (ϵ 4400) nm; ^{13}C NMR ($CDCl_3$) δ 29.5, 40.2, 124.5, 127.0, 127.6, 128.2, 130.4, 131.7, 132.8, 135.3, 135.6, 161.0, 200.6 ppm; measured mass 341.1611 (rel intensity 86.5%), calcd mass 341.1599 (dev 1.2 mmass units).

Characterization of 2-*tert*-Butyl-3,3-dimethylbenzoazasilole. A colorless liquid, 2.22 g (10.2 mmol, 53%), was obtained: bp 86–88 °C (0.35 mm); IR ($CHCl_3$) 3050 (w), 2940 (s), 1645 (w), 1590, 1565 (w) cm^{-1}; ^1H NMR (CCl_4) δ 0.39 (s, 6 H), 1.24 (s, 9 H), 7.0–7.5 (m, 4 H); UV (CCl_4) 255 (ϵ 3500), 273 (ϵ 3600), 302 (ϵ 3600) nm; ^{13}C NMR −2.9, 28.7, 39.7, 124.1, 126.4, 129.3, 131.1, 131.4, 159.6, 201.7 ppm; measured mass 217.1284 (rel intensity 53.1%), calcd mass 217.1287 (dev. 0.3 mmass unit).

Characterization of 2-*tert*-Butyl-3,3-dimethylbenzoazagermole. A slightly yellow, viscous oil, 3.46 g (13.2 mmol, 68%), was obtained: bp 71–74 °C (0.01 mm); IR (CCl_4) 3050 (m), 2950 (s), 1940 (w), 1905 (w), 1835 (w), 1805 (w), 1600 (m) cm^{-1}; ^1H NMR δ 0.59 (s, 6 H), 1.23 (s, 9 H), 7.0–7.6 (m, 4 H); UV (CCl_4) 253 (ϵ 4600), 265 (ϵ 4600) 293 (ϵ 3400) nm; ^{13}C NMR ($CDCl_3$) δ −1.6, 28.7, 40.5, 118.6, 124.8, 126.6, 128.6, 130.1, 131.4, 161.5, 201.3 ppm; measured mass 263.0714 (rel. intensity 30.3%), calcd mass (based on Ge, 36% abundance) 263.0729 (dev. 1.5 mmass units).

Characterization of 2-*tert*-Butyl-3,3-dimethylbenzoazastannole. A yellow viscous oil, 2.46 g (8.0 mmol, 41%), was obtained: bp 80–82 °C (0.01 mm); IR (CCl_4) 3050 (m), 2950 (s), 1940 (w), 1905 (w), 1840 (w), 1805 (w), 1595 (m) cm^{-1}; ^1H NMR (CCl_4) δ 0.52 (s, 6 H, ^{117}Sn, J = 62 Hz, ^{119}Sn, J = 66 Hz), 1.18 (s, 9 H), 7.0–7.7 (m, 4 H); UV (CCl_4) 252 (ϵ 6100), 256 (ϵ 6100) 294 (ϵ 3800) nm; ^{13}C NMR ($CDCl_3$) δ −7.1, 28.8, 41.7, 119.4, 126.0, 126.6, 127.1, 128.9, 130.1, 135.4, 159.6; measured mass 309.0560 (rel. intensity 25.9%), calcd mass (based on ^{120}Sn, 33% abundance) 309.0537 (dev. 2.3 mmass units).

Registry No.—**2** (R = *t*-Bu), 64414-13-7; **10**, 6441401206; **11**, 64414-11-5; **12**, 6625-74-7; *tert*-butyllithium, 594-19-4; phenyl isocyanide, 931-54-4; methyl iodide, 74-88-4; methyl *tert*-butyl ketone, 75-97-8; methyl *tert*-butyl ketone oxime, 2475-93-6; 2-oxo-3,3-dimethylbutanoic acid, 815-17-8; anthranilic acid, 118-92-3; *N*-(1-copper-2,2-dimethylpropylidene)benzenamine, 64414-10-4; cuprous chloride, 7758-89-6; *N*-(2,2-dimethylpropylidene)benzenamine, 26029-60-7; SCl_2, 10545-99-0; $PhPCl_2$, 644-97-3; $(Ph)_2SiCl_2$, 80-10-4; Me_2SiCl_2, 75-78-5; Me_2GeCl_2, 1529-48-2; Me_2SnCl_2, 753-73-1.

References and Notes

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Notes

Isocyanide–Metal Exchange.[1] The Synthesis of Masked Acyl Cyanides

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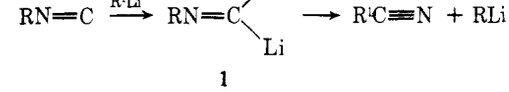
Received August 1, 1977

During the investigation of the synthetic utility of lithium aldimines (**1**), formed by the addition of alkyllithium reagents to isocyanides,[2] it was discovered that a number of them dissociated to produce cyanides in very good yields.[3] A detailed study of the isocyanide–metal exchange reaction showed that



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both steric and electronic effects play a role in the dissociation mechanism. Synthetically, this reaction provided a convenient route to the preparation of nitriles from lithium reagents. The use of the isocyanide–metal exchange reaction for the preparation of masked acyl cyanides is the subject of this report.

The reaction of lithium aldimine (**2**), prepared by lithiation of 1,1,3,3-tetramethylbutyl isocyanide (TMBI) with triphenylmethyl isocyanide, gave the masked acyl cyanide **3**. The

0022-3263/78/1943-0734$01.00/0