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## 27. CYCLOMETALLATED ORGANOLITHIUM COMPOUNDS

Submitted by JOHANN T. B. H. JASTRZEBSKI\* and GERARD VAN KOTEN\*  
Checked by M. F. LAPPERT,<sup>†</sup> P. C. BLAKE,<sup>†</sup> and D. R. HANKEY<sup>†</sup>

Cyclometallated organolithium compounds with one σ C—Li bond and at least one heteroatom—Li bond are valuable starting materials in organometallic<sup>1</sup> and organic synthesis.<sup>2</sup> These organolithium species are made either by a lithium—halogen exchange reaction<sup>3,4</sup> or via direct metallation when activating ligands such as tetramethylethylenediamine (tmeda) are used.<sup>5</sup> Further reactions are mostly carried out with the solutions or suspensions prepared *in situ*. This is, however, a great disadvantage in organometallic synthesis since other species present (R—X, LiX, tmeda, etc.) can either react further with the desired organometallic product (thereby lowering the yield) or hamper product isolation.

We describe here a series of organolithium compounds that can be prepared easily as pure crystalline solids. The synthesis involves a heteroatom assisted lithiation reaction<sup>6</sup> of the parent hydrocarbon using butyllithium and can, moreover, be scaled up without difficulty.

Under an inert atmosphere these extremely air-sensitive compounds are, in contrast to their solutions, almost indefinitely stable. The recording of

\*Laboratory of Organic Chemistry, University of Utrecht, Dept. Metal Mediated Synthesis Padualaan 8, 3584 CH, Utrecht, The Netherlands.

<sup>†</sup>School of Chemistry and Molecular Science, University of Sussex, Brighton, BN1 9QJ, United Kingdom.

$^1\text{H}$  NMR spectra in suitable solvents (see procedures) under an  $\text{N}_2$  atmosphere provides the best method of checking their purity.

The organolithium compounds described here have proved to be valuable in the synthesis of a wide range of cyclometallated compounds, many of which are of current interest.<sup>7</sup> The precise site of lithiation in these reagents has been determined from investigations of the air-stable products that they form with  $\text{Me}_3\text{SiCl}$  and  $\text{Me}_3\text{SnCl}$ .<sup>8</sup>

### General procedure

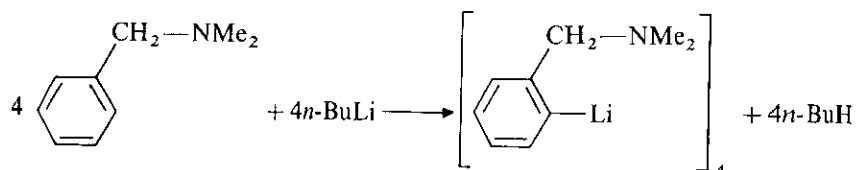
■ **Caution.** Organolithium compounds are extremely air and moisture sensitive and therefore all manipulations described here should be carried out under a dry nitrogen atmosphere using Schlenk-tube techniques.<sup>9</sup> Solvents are dried preferably with sodium metal and distilled under nitrogen. Pure isolated organolithium compounds are pyrophoric in air.

The following detailed procedure is appropriate for the preparation and isolation of all the organolithium compounds on a 25-mmol scale. Precise information concerning reaction times, temperatures, quantity of reagents, and so on is given later for each specific synthesis.

A 100-mL Schlenk tube, fitted with a rubber serum cap and containing a magnetic stirring bar, is connected to a standard nitrogen gas-vacuum pump system and filled with nitrogen. Using syringe techniques the amine (which has been distilled and stored under  $\text{N}_2$ ) is added to the Schlenk tube followed by solvent(s) and a solution of butyllithium in hexane. An  $\sim 2.5\text{ M}$  solution of butyllithium in hexane is obtainable from Aldrich. Before each synthesis the molarity of the solution is determined by methods described in Ref. 10. It is advised that the mixture be stirred until the reaction is complete, in order to prevent formation of the desired lithium product as large crystals which have reduced reactivity. In most preparations the product will then precipitate. However, in the case that it does not, the solvent and volatiles should be removed *in vacuo*. Pentane is added to form a suspension. The serum cap is removed and replaced by a joined glass frit filter (15–40  $\mu$ , about 3 cm in diameter) fitted with a vacuum tap on each side of the frit and connected to a second Schlenk tube. During this exchange, two strong streams of nitrogen are led through the system in order to ensure exclusion of air. Inversion of the whole system allows filtration of the mixture and, while keeping the solid under nitrogen, the upper (reaction) Schlenk tube is removed, the solid washed with pentane (3  $\times$  10 mL), and a storage Schlenk tube connected to the filter. The lower Schlenk tube containing the mother liquor and washings is removed and the frit is closed by a rubber stopper. Then the solid product left on the filter, is dried *in vacuo*. Finally, the system is inverted again so that the dry material can be easily transferred to the storage Schlenk tube.

■ **Caution.** Residual organolithium either in solution or on the filter should be carefully decomposed under nitrogen with a toluene-ethanol 10:1 mixture.

#### A. [2-[(DIMETHYLAMINO)METHYL]PHENYL]LITHIUM



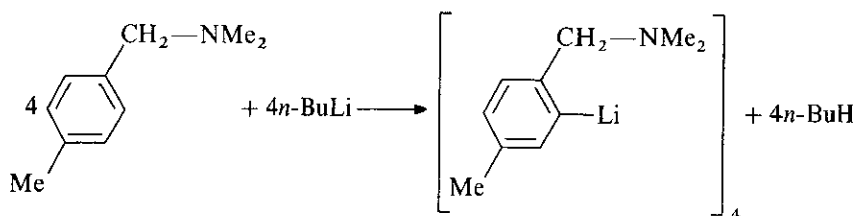
#### Procedure

This is a modification of the methods by Hauser and coworkers<sup>3</sup> and Viswanathan and Wilkie.<sup>11</sup> Following the general procedures just described, *N,N*-dimethylbenzylamine (3.37 g, 25 mmol) is allowed to react in diethyl ether (50 mL) with  $\sim 2.5 M$  of butyllithium in hexane (25 mmol,  $\sim 10$  mL) for 36 h at room temperature after which the product is filtered off. **Yield:** 3 g (87%). <sup>1</sup>HNMR in THF-*d*<sub>8</sub> ( $\delta$  ppm): NMe<sub>2</sub> 2.10 (6H), NCH<sub>2</sub> 3.40 (2H), H<sub>6</sub>(aryl) 7.90 (1H) and other aryl-H 6.80 m (3H).

#### Properties

[2-[(Dimethylamino)methyl]phenyl]lithium is a white crystalline solid and pyrophoric in air. An X-ray structure determination reveals a tetranuclear structure in which each aryl moiety is four-center two-electron bound via C-1 to one Li<sub>3</sub> face of a Li<sub>4</sub> tetrahedron. The remaining free coordination site on each Li atom is occupied by the heteroatom containing substituent CH<sub>2</sub>(Me<sub>2</sub>)N.<sup>12</sup> It is insoluble in hydrocarbons and diethyl ether, but very soluble in THF in which the tetramer breaks down into a dimeric species containing two three-center two-electron bound aryl groups. This was established by <sup>13</sup>CNMR in THF-*d*<sub>8</sub> showing the resonance of C-1 as a seven line pattern arising from coupling to two equivalent <sup>7</sup>Li (*I* =  $\frac{3}{2}$ ) atoms.<sup>12,14</sup>

#### B. [2-[(DIMETHYLAMINO)METHYL]-5-METHYLPHENYL]-LITHIUM

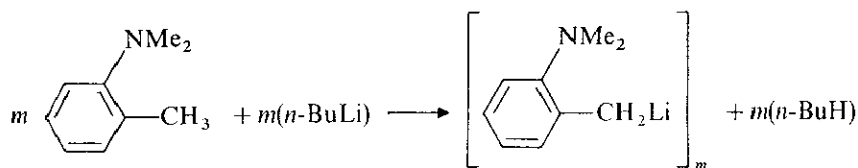


*Procedure*

Following the general procedures just described, *N,N*-4-trimethylbenzylamine (3.73 g, 25 mmol) in diethyl ether (50 mL) is allowed to react with  $\sim 2.5$  M of *n*-butyllithium in hexane (25 mmol,  $\sim 10$  mL) for 36 h at room temperature. After evaporating the solution *in vacuo* and adding pentane (20 mL) the solid is filtered off. Yield: 3 g (77%).  $^1\text{H NMR}$  in  $\text{C}_6\text{D}_6$  ( $\delta$  ppm):  $\text{NMe}_2$  1.30 (3H) and 1.90 (3H);  $\text{NCH}_2$  AB pattern 2.95 (1H) and 4.50 (1H),  $J_{\text{AB}}$  12 Hz;  $\text{Me}(\text{aryl})$  2.30 (3H);  $\text{H}_6(\text{aryl})$  8.15 (1H), other aryl-H 7.00 (2H).

*Properties*

[2-[(Dimethylamino)methyl]-5-methylphenyl]lithium is a white crystalline solid and is pyrophoric in air. Furthermore, it is soluble in hydrocarbons and ethers. Molecular weight determinations in benzene have established a tetrameric structure.<sup>12</sup> In THF, like [2-[(dimethylamino)methyl]phenyl]lithium, this tetramer breaks down to a dimeric species.

**C. [2-[(DIMETHYLAMINO)PHENYL]METHYL]LITHIUM***Procedure*

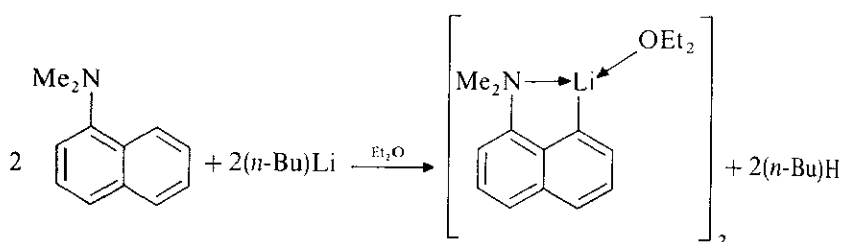
This is a modification and extension of the preparation given by Manzer.<sup>13</sup> Using the general procedures just described, a quantity of *N,N*-2-trimethylaniline (3.37 g, 25 mol) is placed in a Schlenk tube, and to this is added hexane (50 mL), diethyl ether (2 mL), and  $\sim 2.5$  M of butyllithium in hexane (24 mmol,  $\sim 10$  mL). The serum cap is replaced by a reflux condenser, which is connected to a nitrogen gas line and an oil bubbler that is suitably designed to prevent build up of internal pressure. The mixture is refluxed for 10 h. After cooling to room temperature, the precipitate is filtered off under inert atmosphere. Yield: 2.8 g (79%).  $^1\text{H NMR}$  in  $\text{THF-}d_8$  ( $\delta$  ppm):  $\text{NMe}_2$  2.50 (6H);  $\text{CH}_2\text{Li}$  1.48 (2H); aryl-H 5.65 (1H), 6.30 (2H) and 7.00 (1H).

*Properties*

[2-[(Dimethylamino)phenyl]methyl]lithium is a pale yellow crystalline solid pyrophoric in air that is insoluble in hydrocarbons but readily soluble in THF.

To date there is little information concerning the nuclearity of this Li compound either in solution or in the solid state.

#### D. (DIETHYL ETHER)[8-(DIMETHYLAMINO)-1-NAPHTHYL]LITHIUM



#### Procedure

Using the general procedure just described, *N,N*-dimethyl-1-naphthaleneamine (4.28 g, 25 mmol) in diethyl ether (40 mL) is reacted with a  $\sim 2.5$  M hexane solution of butyllithium (25 mmol,  $\sim 10$  mL) at room temperature for 36 h after which the product is filtered off. Yield: 4.3 g (70%).  $^1\text{H}$  NMR in  $\text{C}_6\text{D}_6$  ( $\delta$  ppm):  $\text{Me}(\text{Et}_2\text{O})$  1.05 (6H);  $\text{CH}_2(\text{Et}_2\text{O})$  3.20 (4H);  $\text{NMe}_2$  1.95 (6H); Aryl-H 7.05 (2H), 7.30 (1H), 7.65 (2H) and 8.15 (1H).

#### Properties

(Diethyl ether)[8-(dimethylamino)-1-naphthyl]lithium is a very oxygen- and moisture-sensitive yellow crystalline solid. An X-ray structure determination<sup>14</sup> reveals a dimeric complex in which each of the 8-(dimethylamino)-1-naphthyl groups is bound to two Li atoms via C-1 and via the lone pair of the  $\text{NMe}_2$  nitrogen atom, to one of these Li atoms. The fourth coordination site of each Li atom is occupied by a coordinated diethyl ether molecule.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^7\text{Li}$  NMR studies<sup>12,14</sup> indicate that in solution an equilibrium exists between the dimeric diethyl ether complex and an ether-free organolithium species whose structure and aggregation is still under investigation. This white, ether-free species can be isolated as a microcrystalline solid in almost quantitative yield by simply removing the solvent *in vacuo* from a benzene solution of the etherate.

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## 28. METALLATION OF AROMATIC KETONES WITH PENTACARBONYLMETHYLMANGANESE(I)

Submitted by R. J. MCKINNEY\* and S. S. CRAWFORD\*

Checked by K. OBERDORF<sup>†</sup> and J. L. SPENCER<sup>†</sup>

The internal metallation of aromatic groups on ligands of transition metal complexes has been the subject of widespread studies primarily because of interest in C—H activation.<sup>1,2</sup> Most studies have involved either nitrogen or phosphorus donor ligands, whereas very few have explored metallation with oxygen donor ligands. Perhaps this disparity may be traced to the relatively weak bonding interaction of oxygen-donor ligands in general towards late transition metal complexes as compared to nitrogen and phosphorus-donor

\*Department of Chemistry, University of California, Los Angeles, CA 90024. Present Address for R. J. McKinney: Central Research & Development Department, E. I. du Pont de Nemours & Company, Experimental Station, Wilmington, DE 19880-0328.

<sup>†</sup>Department of Inorganic Chemistry, University of Bristol, Bristol BS8 1TS, United Kingdom.