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Aryllithiums with Increasing Steric Crowding and Lipophilicity Prepared from Chlorides in Diethyl Ether. The First Directly Prepared Room-Temperature-Stable Dilithioarenes

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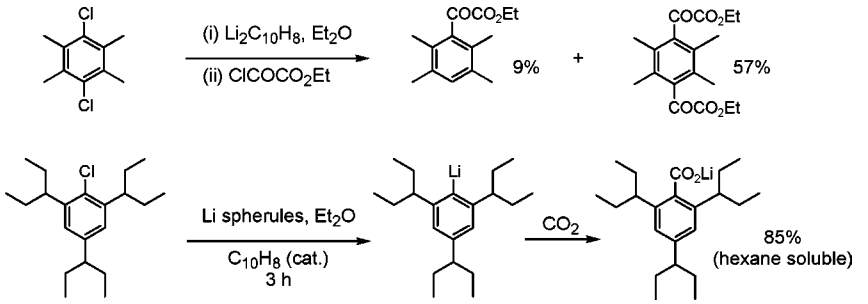
ABSTRACT



A convenient procedure has been developed for the preparation of synthetically useful, room-temperature-stable aryllithiums starting from aryl chlorides and lithium metal. The method provides a route to aryllithiums which have previously not been accessible cleanly or could only be prepared by using more expensive starting materials.

The introduction of alkyl-substituted aryl groups is often required for the synthesis of functional compounds or materials intended for special applications. For example, molecules with sterically hindered coordination sites are frequently employed as ligands in catalysis,[1] while

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bulky alkyl-substituted aryl groups are commonly used to stabilize compounds with unusual valency or low oxidation states.[2] In organic synthesis, an example of their utility is the α-lithiation of highly hindered benzoate esters to provide lithioalkyl alcohol synthons.[3] They may also render requisite lipophilicity to biologically active molecules or contribute to space-filling requirements for effective functioning.[4] There is therefore a need for versatile synthetic methodologies for the functionalization of polyalkylated arenes, particularly where conventional aromatic substitution routes fail to give satisfactory results due to rearrangement, disproportionation, or loss of alkyl groups.[5] This issue can be a more serious problem for secondary or tertiary alkyl groups and in these cases special conditions must often be employed.[6]

A possible synthetic route to the desired derivatives is via appropriate organolithiums. The commonly used method for the preparation of aryllithiums (ArLi) is by halogen–metal exchange, usually from the corresponding bromides.[7] The generation of ArLi directly from the metal is seldom employed, and it is notable that the majority of direct routes to ArLi in the comprehensive compilation by Schlosser also start from the bromides.[8] The use of chlorides in the direct synthesis of ArLi by reductive lithiation in THF is known but it requires low to very low reaction temperatures.[9] Conversion of chlorides to polyalkylated phenyllithiums, in particular, remains somewhat unexplored although there is a considerable cost benefit and many chlorides are also readily prepared by chlorinating the corresponding hydrocarbons by the method of Hojo and Masuda.[10]

Although simple aryl chlorides react readily with lithium chips in THF, the reaction appears to be complicated, judging from the plethora of species formed upon derivatization. Problems may arise from benzyne formation as a result of the ortho-directing ability of the chlorine substituent,[11] or the activation of the metalating ability of the initial ArLi by THF which is a relatively strong Lewis base.[12] For polymethylated chlorobenzenes, the electronegative substituent also enhances the carbon acidity of adjacent methyls leading to complications due to the formation of benzylic carbanions. Another problem associated with THF in the conversion of aryl chlorides and sulfides[13] of *pronounced electron affinity* to ArLi is that they form stable radical anions which either do not undergo carbon–heteroatom bond fission (a prerequisite for lithiative cleavage[14]) or follow other pathways. We reasoned that Et_2O, which exhibits a very low Lewis basicity, would be a better medium for the direct synthesis of ArLi from chlorides. It has been shown to be appropriate for the cleavage of allylic phenyl sulfides,[15] and phenylthioalkanes (under catalysis by naphthalene)[16] to provide organolithium reagents. It may also be noted that methyl *tert*-butyl ether has been used as an additive in the preparation of secondary and tertiary alkyllithiums from the chlorides in pentane.[17]

In Et_2O, aryl chlorides react slowly with Li chips but very rapidly with Li dispersion. The use of Li dispersion, however, presents some difficulties. Weighing milligram quantities, for example, requires an inert atmosphere. Here we report a simple method for the preparation of a form of lithium with a particle size ranging from about 0.3 mm down to the size of Li dispersion. These are formed by addition of Li pieces under argon to warm mineral oil containing a small amount of cholesterol and then heating to 210–230 °C with vigorous magnetic stirring. After cooling, removal of the oil and then washing with hexane leaves shiny particles of Li metal. Their size was determined by measurement under a microscope of the larger particles and comparison of the smallest particles with those from a lithium dispersion. This form of Li can be handled briefly in air and is active enough so that, upon contact with a dilute solution of naphthalene in Et_2O, it begins to reduce it to the dianion within 20–30 s. Since this form of the metal is distinctly different from Li shot,[18] we use the term *lithium spherules*.

Starting from the chlorides, we have synthesized a series of ArLi with increasing numbers of methyl and 2-ethylpropyl groups as well as the 1,3,5-triisopropylphenyl derivative. We also studied the dichlorides of mesitylene and durene as well as some chloronaphthalenes and chlorostilbenes. In special cases, preformed dilithium naphthalene dianion in Et_2O was employed as the source of Li. As electrophiles we have applied CO_2, paraformaldehyde, DMF, $ClCO_2Et$, and $ClCOCO_2Et$, the last being of interest since, not only does it provide a method of acylation where conventional electrophilic acylation may not applicable, but also because the

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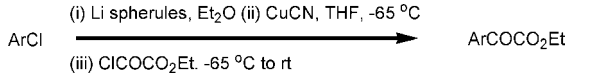
α-ketoesters produced are precursors for interesting and useful α-amino acids[19] or α-hydroxy acids.[20]

Chlorotoluenes react readily with Li spherules in Et_2O at ice bath temperatures (3−6 °C) and afford tolyllithiums in high yields (Table 1) within 1−3 h, while for Li chips up to 20 h are needed for comparable results. Additional methyls do not cause any appreciable drop in reactivity and the chloroxylenes, chloromesitylene, chlorodurene and chloropentamethylbenzene gave similar results. Entries 7 and 9 in Table 1 indicate the long-term stability of the organolithiums in solution. These results may be contrasted with those using THF. Reaction of mesityl chloride with Li chips and derivatization with allyl bromide gave 3 major products: mesitylene, 35%, 2,4,6-trimethylallylbenzene, 40%, and 1-chloro-2-buten-3-yl-4,6-dimethylbenzene, 14%, along with 12 minor products.

The presence of three isopropyl or two 1-ethypropyl groups in the ring considerably diminishes the reactivity toward lithium spherules in Et_2O. In these cases, however, catalysis by naphthalene was found to reduce the reaction time to 3−4 h (Table 2).

Table 1. Reaction of Aryl Chlorides with Li Spherules in Et_2O

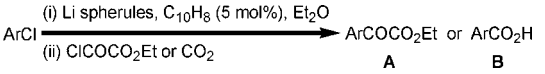


entry	Ar	temp (°C)	time[a] (h)	yield[b] (%)
1	2-tolyl	3−6	3	91
2	3-tolyl	3−6	3	86
3	4-tolyl	3−6	3	95
4	2,6-dimethylphenyl	3−6	3.75	99
5	2,5-dimethylphenyl	3−6	4.5	95
6	2,4,6-trimethylphenyl	3−6	3	99
7	2,3,5,6-tetramethylphenyl	rt	22	77
8	pentamethylphenyl	rt	4	86
9	pentamethylphenyl	rt	22	81
10	3,4-bis(1-ethylpropyl)phenyl	rt	19	80
11	2,4,6-tris(1-ethylpropyl)phenyl	rt	23	0[c]

[a] Reaction time for formation of organolithium. [b] Isolated yields. [c] 77% of starting material recovered.

1-Chloro-2,4,6,-tris(1-ethylpropyl)benzene gave good yields only under catalysis with naphthalene (Table 2, entries 9 and 10). In the uncatalyzed reaction, 73% of the aryl chloride was recovered unchanged after 23 h at room temperature, while the remainder was dehalogenated to the hydrocarbon (Table 1, entry 11). Complete dehalogenation takes place even under catalysis for longer reaction times, indicating that 2,4,6-tris(1-ethylpropyl)phenyllithium is not very stable at room temperature (Table 2, entry 8). This reagent reacts in Et_2O with gaseous CO_2 to give a hexane-soluble lithium 2,4,6-tris(1-ethylpropyl)benzoate. After hydration, this highly lipophilic salt is no longer re-extractable into hexane.

Table 2. Naphthalene-Catalyzed Direct Lithiation of Substituted Chlorobenzenes

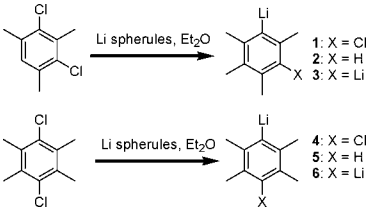


entry	Ar	temp (°C)	time (h)	product	yield[a] (%)
1	pentamethylphenyl	rt	4	**A**	86
2	2,3,5,6-tetramethylphenyl	3−6	3	**A**	98
3	3,4-bis(1-ethylpropyl)phenyl[b]	3−6	1.5	**A**	67
4	2,4-bis(1-ethylpropyl)phenyl[b]	3−6	4	**A**	76
5	2,5-bis(1-ethylpropyl)phenyl[b]	3−6	3	**A**	65
6	2,4,6-triisopropylphenyl	3−6	2	**B**	91
7	2,4,6-triisopropylphenyl	3−6	2.5	**A**	86
8	2,4,6-tris(1-ethylpropyl)phenyl	rt	23	**A**	0
9	2,4,6-tris(1-ethylpropyl)phenyl	3−6	3[c]	**B**	85
10	2,4,6-tris(1-ethylpropyl)phenyl	3−6	3[c]	**A**	60

[a] Isolated yields. [b] CuCN added to organolithium prior to addition of electrophile. [c] 2 h at 3−6 °C + 1 h at rt.

1,3-Dichloro-2,4,6-trimethylbenzene and 1,4-dichloro-2,3,5,6-tetramethylbenzene react with Li spherules to give mixtures of 3 possible products (Scheme 1) which were inferred by conversion to the oxoaceates and analyzed by GC-MS. Obviously the stability of **1** and **3**, as well as **4** and **6**, is due to the fact that the halogen or lithium substituents are flanked by methyl groups which preclude benzyne formation. These constitute the first examples of the generation of room temperature stable solutions of methyl-substituted dilithiobenzenes *directly* from chlorides. Previous reports have involved bromides and iodides and halogen−metal interconversion.[21]

Scheme 1. Direct Lithiation of Aryl Dichlorides



The reaction of the dichlorides with preformed dilithium naphthalene dianion[22] leads to the dilithiated and dehalomonolithiated products **2**, **3** and **5**, **6** (Table 3). 1-Chloro-2,4,6-tris(1-ethylpropyl)benzene could also be converted in good yield by this route (Table 3, entry 1).

(20) For recent examples, see: (a) Pennacchio, A.; Rossi, M.; Raia, C. A.; Giordano, A. *Eur. J. Org. Chem.* **2011**, 4361. (b) Ni, Y.; Li, C.-Y.; Wang, L.-J.; Zhang, J.; Xu, J.-H. *Org. Biomol. Chem.* **2011**, *9*, 5463. (c) Balazsik, K.; Szri, K.; Gyoergy, B. M. *Chem. Commun.* **2011**, *47*, 1551.

(21) Fossatelli, M.; den Besten, R.; Verkruijsse, H. D.; Brandsma, L. *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 527and references therein.

(22) Dilithium naphthalene dianion in Et_2O appears to be quite stable at room temperature, in contrast to the situation with THF. See: Yus, M.; Herrera, R. P.; Guijarro, A. *Chem.—Eur. J.* **2002**, *8*, 2574. Yus, M.; Herrera, R. P.; Guijarro, A. *Tetrahedron Lett.* **2001**, *42*, 3455.

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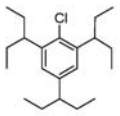
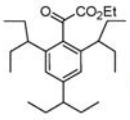
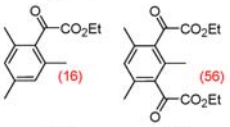
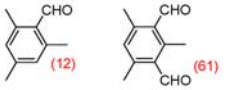
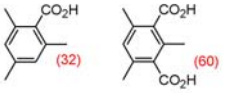
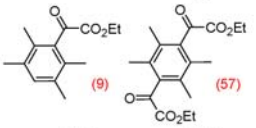
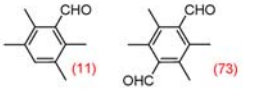
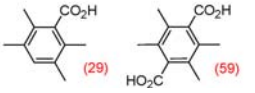
Table 3. Reactions with Dilithium Naphthalene Dianion

Reaction conditions: (i) $Li_2C_{10}H_8$, Et_2O, r.t. (ii) CO_2, $ClCOCO_2Et$ or DMF

entry	aryl (di)chloride	electrophile	product(s) (yield %)
1		$ClCOCO_2Et$	 (81)
2		$ClCOCO_2Et$	 (16) (56)
3		DMF	 (12) (61)
4		CO_2	 (32) (60)
5		$ClCOCO_2Et$	 (9) (57)
6		DMF	 (11) (73)
7		CO_2	 (29) (59)

Reports on the synthesis of 1-naphthyllithium from 1-chloronaphthalene are scarce,[23] while no analogous report was found for 2-naphthyllithium. 1-Chloronaphthalene reacts readily with Li spherules in Et_2O with apparent rapid dissolution of the metal and after 2−3 h at room temperature affords fair yields of 1-naphthyllithium (Table 4, entry 1). The dissolution of the metal and the initial purple color of the solution suggest the intermediacy of the 1-chloronaphthalene dianion. This is favored by the poor solvating ability of Et_2O; it is known that addition of the weakly solvating Et_2O or Et_3N to THF solutions of alkali metal naphthalene radical anions causes disproportionation to naphthalene and its dianion.[24]

2-Chloronaphthalene gave poor yields of 2-naphthyllithium (entry 2), and considering its high price, we sought alternative starting materials for the synthesis of 2-naphthyllithium and examined the lithiative cleavage of 2-phenylthionaphthalene, 2-methoxynaphthalene, 2-trimethylsilyloxynaphthalene, tri-2-naphthyl phosphate, and 2-naphthyl tosylate. Of these, only the PhS and MeO derivatives reacted with Li spherules in Et_2O to give fair yields of 2-naphthyllithium. The cleavage of 2-methoxynaphthalene to 2-naphthyllithium and LiOMe rather than to MeLi and lithium 2-naphthoxide is somewhat unexpected. Assuming that the C−O cleavage reaction path is governed by the thermochemical stability of the fragments,[13] this result

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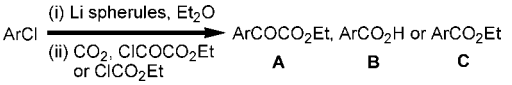
Table 4. Aryllithiums from Chloronaphthalenes and Chlorostilbenes in Et_2O[a]



entry	Ar	time (h)	product	yield (%)
1	1-naphthyl[b]	3	**A**	72
2	2-naphthyl	3	**B**	28
3	1-(2-methyl)naphthyl	4	**A**	53
4	1-(4-methyl)naphthyl	4	**A**	35
5	1-(2-methoxy)naphthyl	2	**A**	82
6	1-(2-methoxy)naphthyl	3	**B**	80
7	(5,6,7,8-tetrahydro)naphthyl[c]	2.5	**B**	88 (40/48)[d]
8	2-styrylphenyl	20	**C**	76
9	2-styrylphenyl	20	**B**	70
10	3-styrylphenyl	3	**B**	78
11	4-styrylphenyl	22	**C**	[e]

[a] All reactions carried out at rt unless otherwise stated. [b] Contained 13% 2-chloronaphthalene. [c] 40/60 mixture of 1- and 2-isomers. Reaction carried out at 3−6 °C with prior formation of cuprate. [d] GC yields. [e] Very complex mixture.

may arise because the pK_a of MeOH is lower than that of 2-naphthol in Et_2O.

Methyl and methoxy derivatives of 1-chloronaphthalene were also investigated. 1-Chloro-2-methylnaphthalene gave good yields of 1-lithio-2-methylnaphthalene (entry 3), while 1-chloro-4-methylnaphthalene gave rather low yields of the corresponding naphthyllithium (entry 4). 1-Chloro-2-methoxynaphthalene reacted cleanly and afforded good yields of 1-lithio-2-methoxynaphthalene (entries 5,6). Obviously this is due to the difference in cleavability between C−Cl and C−O bonds in favor of the former. An approximately 40−60% mixture of 1- and 2-chlorotetralin gave a good overall yield of the corresponding ArLi which were characterized as ethyl 2-oxoacetates (entry 7). We also investigated the chlorostilbenes which tend to form radical anions and dianions even more readily. Indeed, 2-chloro- and 3-chlorostilbenes reacted with Li spherules in Et_2O to afford good yields of the corresponding lithiostilbenes (entries 8−10) although 4-chlorostilbene only gave a complex mixture of products (entry 11). It is stressed that 2-phenylthio- and 2-methoxynaphthalene as well as the chloronaphthalenes and chlorostilbenes fail to react *cleanly* with Li in THF for reasons already mentioned.[13]

In conclusion, we have developed a convenient procedure for the preparation of synthetically useful, room temperature stable aryllithiums which have previously not been accessible cleanly or only by using more expensive starting materials.

Supporting Information Available. Full experimental details, mass spectra, and ^1H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.