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Partially fluorinated naphthalene derivatives from 1,4-dilithio-1,3-dienes and C_6F_6

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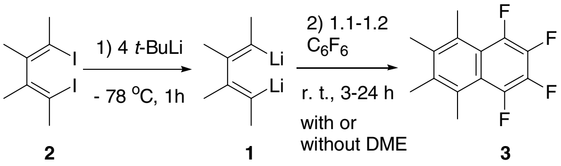
Abstract—Multi-substituted partially fluorinated aromatic compounds, such as naphthalene derivatives could be readily prepared by the reaction of 1,4-dilithio-1,3-dienes with hexafluorobenzene via double nucleophilic substitution. When these dilithium reagents were treated with hexachlorobenzene, chloropentafluorobenzene or bromopentafluorobenzene, chlorine–lithium or bromine–lithium exchange reactions, instead of nucleophilic substitution, took place.

Aromatic π-stacking interaction is widespread in nature and is one of the most important subjects in supramolecular chemistry.[1] Especially, fluorinated aromatic compounds show unique stacking fashion.[2,3] Recently, Watson group and Piers group independently reported the synthesis and crystallographic analysis of partially fluorinated condensed aromatic compounds by lithium–bromine exchange of 2,2′-dibromobiaryls and nucleophilic substitutions of aromatic fluorines.[4,5] Anthony and co-workers recently reported the synthesis and characterization of partially fluorinated pentacenes.[6] Takahashi and co-workers have developed synthetic methods of naphthalene derivatives from CuCl-mediated reaction of zirconacyclopentadienes with 1,2-diiodobenzenes.[7,8]

We have been interested in the chemistry and synthetic applications of 1,4-dilithio-1,3-dienes **1**.[9–20] Due our continuing interest in reactions of these di-lithio reagents with multi-functional substrates,[19,20] we investigated the reactions of **1** with C_6F_5X (X = F, Cl, Br), expecting the formation of multi-substituted fluorinated aromatic compounds.[4–6] In this letter, we would like to report the preliminary results.

Reaction of 1,4-dilithio-1,3-dienes **1**, generated in situ from their corresponding diiodo compounds **2**,[10,18,21] with 1.1 or 1.2 equiv of C_6F_6 at room temperature afforded the partially fluorinated naphthalene derivatives **3** in good to high isolated yields (Scheme 1). Intermolecular nucleophilic substitution followed by consequent intramolecular nucleophilic substitution is assumed to be the essential process leading to **3**.[4,5,22,23] Representative examples are given in Table 1. The naphthalene derivatives with different substitution patterns could be prepared conveniently by following the procedure described in Scheme 1. DME was added in some cases to accelerate the reaction process.[24]

It has been reported that fluorinated aromatic compounds show unique π-stacking fashions.[2–5] We subjected naphthalene derivatives **3a** and **3f** to single-crystal X-ray structural analysis to determine their solid-state arrangement, which are shown in Figures 1–3. Figures 1 and 2 represent the structures of **3a** and



Scheme 1.

Keywords: 1,4-Diiodo-1,3-diene; 1,4-Dilithio-1,3-diene; Hexafluorobenzene; Fluorinated naphthalene.

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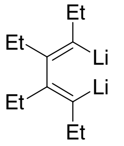
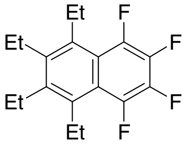
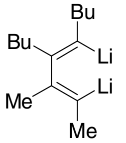
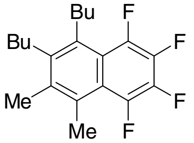
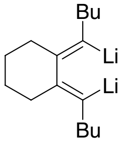
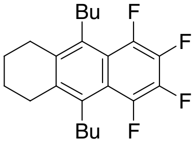
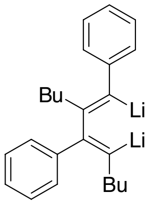
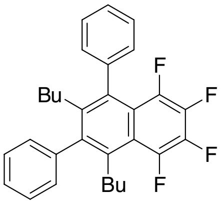
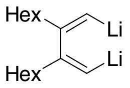
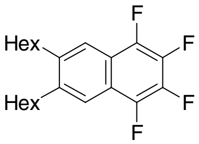
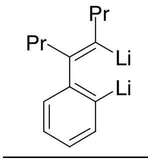
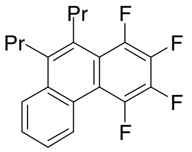
Table 1. Reaction of dilithiobutadienes **1** with C_6F_6 affording partially fluorinated aromatic compounds **3**[a]

Dilithio reagent **1**	Product **3**	Yield[b] (%)
 **1a**	 **3a**	68
 **1b**	 **3b**	54
 **1c**	 **3c**	74
 **1d**	 **3d**	67
 **1e**	 **3e**	72
 **1f**	 **3f**	53

[a] Reaction conditions are given in Scheme 1.

[b] Isolated yields.

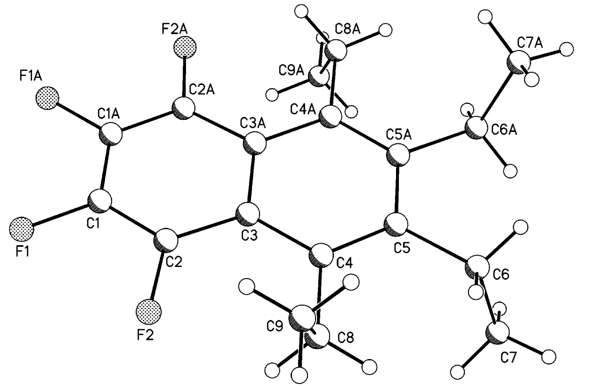


Figure 1. X-ray structure of **3a**.

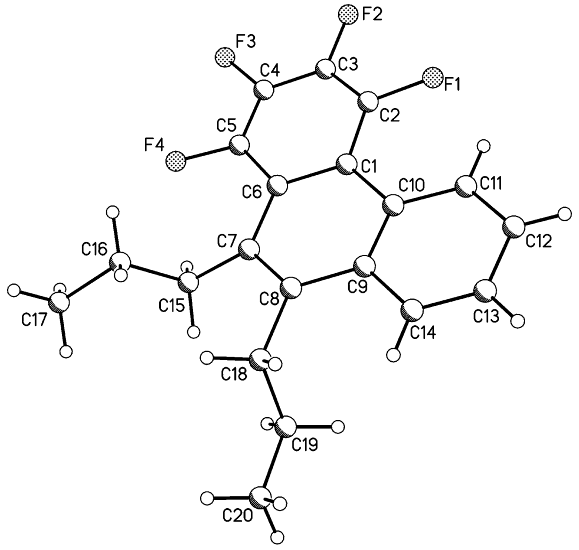
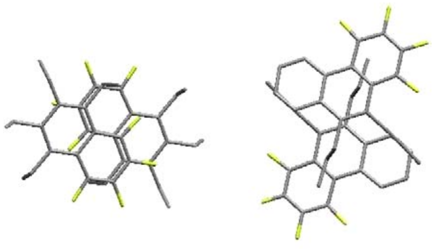


Figure 2. X-ray structure of **3f**.

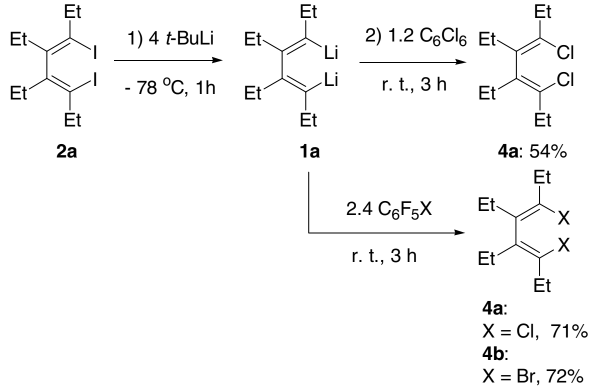


3a **3f**

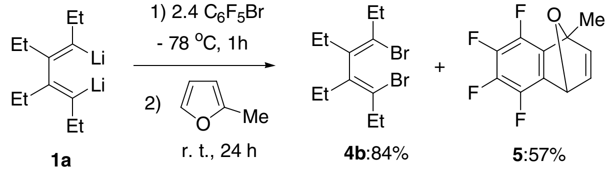
Figure 3. Crystal packing for **3a** and **3f**. Views perpendicular to molecular planes.

3f, respectively,[25] while Figure 3 shows the crystalline packing of **3a** and **3f**. Preliminary results demonstrate that these partially fluorinated multi-substituted naphthalene derivatives also show unique stacking fashions as reported.[4–6] Further applications of these multi-substituted fluorinated aromatic compounds, including study of their opto-electronic materials properties, are in progress.

For comparison of reactivities, C_6Cl_6 was used instead of C_6F_6. Interestingly, no nucleophilic substitution was observed. As shown in Scheme 2, chlorine–lithium ex-



Scheme 2.



Scheme 3.

change reaction took place to afford the 1,4-dichloro-1,3-diene derivative **4a** as the sole product in 54% isolated yield. C_6Cl_6 behaved as a chlorinating reagent.[26–29]

When one of the six fluorines of C_6F_6 was replaced by a chlorine (C_6F_5Cl) or a bromine (C_6F_5Br), the reaction with **1a** afforded its corresponding chlorine–lithium exchange product **4a** or bromine–lithium exchange product **4b**, respectively, in high isolated yields (Scheme 2).[26–29] Upon halogen–lithium exchange between **1a** and C_6F_5X, C_6F_5Li must be formed in addition to **4a** or **4b**. It is known that C_6F_5Li can generate tetrafluorobenzyne species, which can be trapped by dienes via [4+2] cycloaddition.[29] Thus an experiment shown in Scheme 3 was carried out. The [4+2] cycloaddition product **5**,[29e] in addition to **4b** (84% isolated yield), was obtained in 57% isolated yield.

Acknowledgements

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23. A typical procedure for the preparation of **3a** from **1a**: To a solution of 4,5-diethyl-3,6-diiodo-octa-3,5-diene (**2a**) (0.418 g, 1.0 mmol) in THF (5 ml) was added *t*-BuLi (1.5 M pentane solution, 4.0 mmol) at −78 °C and the mixture was stirred for 1 h at the same temperature to generate **1a**. Then hexafluorobenzene (0.205 g, 1.1 mmol) was added, followed by the addition of DME (5 ml), and

stirring was continued at room temperature for 3 h. The reaction mixture was quenched with aqueous $NaHCO_3$ and extracted with ethyl ether. The extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding product **3a**. 1,2,3,4-Tetraethyl-5,6,7,8-tetrafluoro-naphthalene (**3a**). Colorless solid, mp 75–76 °C, isolated yield 68% (212 mg). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.21–1.31 (m, 12H), 2.84 (q, $J = 7.5$ Hz, 4H), 3.13 (q, $J = 7.2$ Hz, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 15.52, 16.04 (m), 22.29, 23.97 (m), 118.97 (m), 133.93 (m), 137.94 (dm, $^1J_{C-F} = 247$ Hz, aryl C–F), 141.03, 143.86 (dm, $^1J_{C-F} = 242$ Hz, aryl C–F). HRMS: calcd for $C_{18}H_{20}F_4$ 312.1501, found 312.1504. Anal. Calcd for $C_{18}H_{20}F_4$: C, 69.22; H, 6.45. Found: C, 69.05; H, 6.55.

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