

(2,3) closely resemble those of BFD (2,3). Based on these observations, we conclude that the  $\pi$ -bridged FDA (2,3) ion is a fully delocalized analogue of BFD (2,3). The question remains as to why BFD (2,3) is a delocalized ion while biferrocene (2,3) is not. Two possible contributing factors in the case of BFD have been cited: the proximity of the iron atoms and the fused  $\pi$ -ligand system. This study shows the importance of the latter.

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## Halogen-Metal Exchange in Esters of Haloaryl Acids<sup>1</sup>

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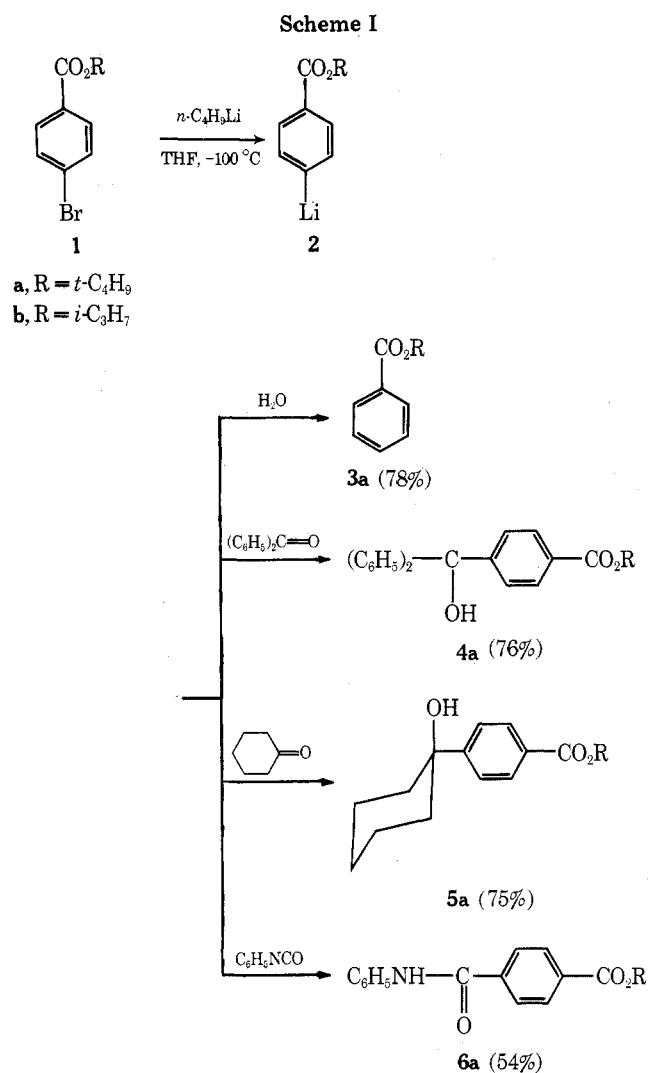
*n*-Butyllithium reacts selectively at  $-100^{\circ}\text{C}$  in THF-hexane with *tert*-butyl *p*-bromobenzoate by halogen-metal exchange; the resulting *tert*-butyl *p*-lithiobenzoate is stable at  $-100^{\circ}\text{C}$  and can be elaborated in high yield to give para-substituted *tert*-butylbenzoates by reactions with electrophiles. The less hindered isopropyl esters are not stable to aryllithium at  $-100^{\circ}\text{C}$  unless further hindered by ortho substitution.

Considerable progress has been made recently in developing improved procedures for the elaboration of aromatic acids utilizing derived aryllithium reagents. The method of Meyers<sup>2</sup> involving direct ortho metalation of oxazolines derived from aromatic acids would appear to be the method of choice for symmetrically substituted 2-aryloxazolines, since the ortho-substituted aryl halide corresponding to the position of lithiation is not a required intermediate as in halogen-metal exchange reactions. The alternative procedure,<sup>3a</sup> developed in our laboratory, involving direct halogen-metal exchange of the lithium salts of bromoarylcarboxylic acids at very low temperature ( $-100^{\circ}\text{C}$ ) affords good yields of elaborated acids, subsequent to reaction with  $\text{E}^+$ . In addition, the process is positionally selective at the site occupied by bromine in the starting acid and is applicable to *o*-, *m*-, or *p*-bromobenzoic acids, as is the complementary procedure employing oxazolines to mask carboxyl functions to Grignard reagents.<sup>4</sup>

It has been shown that stable aryllithium reagents can be prepared at  $-100^{\circ}\text{C}$  with a variety of aryl bromides containing reactive functional groups ( $\text{COO}^-$ ,<sup>3</sup>  $\text{CN}$ ,<sup>5</sup>  $\text{CH}_2\text{Cl}$ ,<sup>6</sup>  $\text{CH}_2\text{CH}_2\text{Br}$ ,<sup>6</sup> *o*- $\text{NO}_2$ ); however, similar reactions<sup>8</sup> with aryl

halides containing methyl ester functions are of limited synthetic utility since the derived aryllithium reagents either self-condense or react with unchanged bromoaryl ester at low temperature ( $-78 \rightarrow -100^{\circ}\text{C}$ ) to give high yields of methyl benzoylbenzoates. In order to further define the limitations for synthetic reactions of aryllithium reagents containing ester functions, we have examined, as model compounds, halogen-metal exchange with *tert*-butyl *p*-bromobenzoate, isopropyl *p*-bromobenzoate, and isopropyl *o*-bromobenzoate. In all cases, progress of halogen-metal exchange was followed by quenching aliquots with water and determining (by NMR, GLC, and isolation of products) the ratio of starting bromoaryl ester to ester derived by replacing bromine with hydrogen.

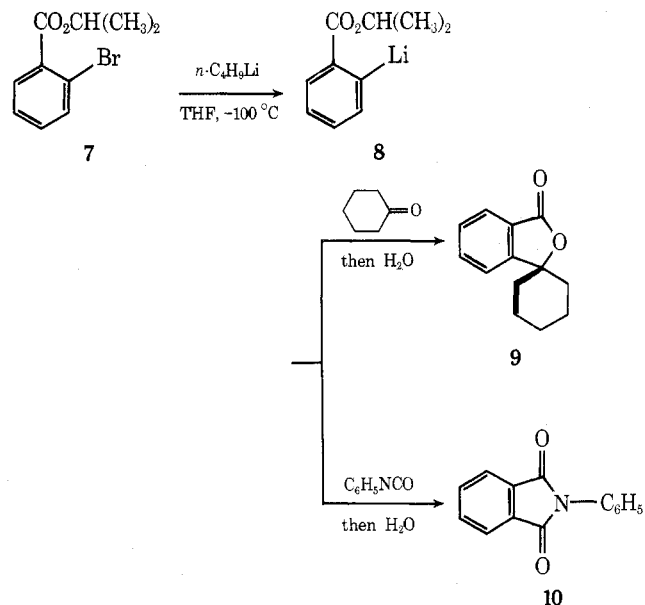
While reaction of *tert*-butyl *p*-bromobenzoate (**1a**)<sup>9</sup> with *n*-propyllithium in ether at  $-40^{\circ}\text{C}$  is reported to involve preferential addition of alkylolithium to the ester function, the reaction of **1a** with *n*-butyllithium in THF-hexane at  $-100^{\circ}\text{C}$  involves selective halogen-metal exchange to give only **2a**. Reaction was complete after 5 min at  $-100^{\circ}\text{C}$ , and good yields (isolated) of elaborated aryl esters were obtained by reaction of **2a** with suitable electrophiles as shown in Scheme I.



While **2a** is stable (during 2-h period examined) at  $-100^\circ\text{C}$ , some loss to condensation products was observed when the solution containing **2a** was warmed to  $-78^\circ\text{C}$  (1 h); extensive reaction occurred to give an unresolved multicomponent mixture (TLC) of presumably higher condensation products when the solution containing **2a** was warmed to  $-20^\circ\text{C}$ .

Reaction of the less hindered ester isopropyl *p*-bromobenzoate (**1b**), under similar conditions with *n*-butyllithium at  $-100^\circ\text{C}$ , was rapid (complete disappearance of **1b** after 5 min); however, a complex mixture of products resulted when the reaction mixture was quenched with water. Products identified were isopropyl benzoate (**3b**, 9% yield), isopropyl (*p*-bromobenzoyl)benzoate (~26% yield), and the carbinol corresponding to addition of *n*-butyllithium to isopropyl (*p*-bromobenzoyl)benzoate (~19% yield, slightly impure) together with considerable material (low  $R_f$ ) assumed to be higher molecular weight condensation products. These products are analogous to, but more complex than, those reported<sup>8</sup> from the corresponding methyl ester of *p*-bromobenzoic acid.

The ester function in isopropyl *o*-bromobenzoate (**7**) is sufficiently hindered to permit complete halogen-metal interchange to give **8**. Studies of aliquots showed only isopropyl *o*-lithiobenzoate (**8**) after 5 min at  $-100^\circ\text{C}$ ; the composition of aliquots taken over a 2-h period at  $-100^\circ\text{C}$  showed no appreciable change. When the solution containing **8** was quenched at  $-100^\circ\text{C}$ , shortly after its formation, with excess cyclohexanone, a mixture was obtained from which the expected lactone **9** was isolated in 43% yield; *N*-phenylphthalimide (**10**) was isolated in 53% yield when the reaction mixture



was quenched with excess phenyl isocyanate. These routes to **9** and **10** are inferior to those previously described from *o*-bromobenzoic acid<sup>3a</sup> or from *o*-bromobenzonitrile.<sup>5</sup> When the solution of **8** was warmed to  $-75^\circ\text{C}$  it decomposed to a complex unresolved mixture, a result in contrast to similar reactions<sup>8</sup> with methyl *o*-bromobenzoate which gave high yields (88%) of methyl *p*-benzoylbenzoate.

In summary, stable aryllithium reagents can be prepared and elaborated in good yields with electrophiles provided that the ester is derived from a tertiary alcohol or is otherwise sterically hindered. These procedures are not only useful for preparation of substituted benzoic esters and acids derived from them, but may offer advantages, in certain cases, to direct use of haloaryl acids, since the lithioaryl esters are generally more soluble at  $-100^\circ\text{C}$  than the corresponding lithioaryl carboxylates.<sup>3a</sup>

### Experimental Section

**Reaction of *tert*-Butyl *p*-Bromobenzoate (**1a**). General Procedure.** 1-(*p*-Carbo-*tert*-butoxyphenyl)cyclohexanol (**5a**). *n*-Butyllithium (7.9 ml, 0.0195 mol, 2.45 M solution in hexane) was added, at a rate such that the temperature did not exceed  $-100^\circ\text{C}$ , to a cold ( $-100^\circ\text{C}$ , liquid nitrogen/diethyl ether bath) mixture of *tert*-butyl *p*-bromobenzoate [NMR ( $\text{CDCl}_3$ )  $\delta$  1.56 (s, 9,  $\text{CH}_3$ ), 7.45 (m, 3, ArH), 8.05 (m, 2, ArH)] (5.0 g, 0.0195 mol), tetrahydrofuran (130 ml, freshly distilled from  $\text{LiAlH}_4$ ), and hexane (35 ml, stored over molecular sieves). The mixture was stirred for 5 min at  $-105^\circ\text{C}$  and cyclohexanone (2.45 g, 0.025 mol) was added at a rate such that the temperature was maintained at  $-98^\circ\text{C}$ . The resulting mixture was stirred for 5 min, allowed to warm to room temperature, and then poured into water (~100 ml). The aqueous layer was extracted with ether. The white solid (5.78 g, mp  $91\text{--}108^\circ\text{C}$ ) obtained from the dried ( $\text{MgSO}_4$ ) ether extract was recrystallized from petroleum ether (bp  $63\text{--}75^\circ\text{C}$ ) to give 5.39 g (75% yield) of **5a** [mp  $128\text{--}129^\circ\text{C}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.60 (s, 9,  $\text{CH}_3$ ), 1.45–2.00 (m, 11, aliphatic H and OH), 7.59 (d, 2, ArH), 7.98 (d, 2, ArH)].

Anal. Calcd for  $\text{C}_{17}\text{H}_{24}\text{O}_3$ : C, 73.88; H, 8.75. Found: C, 73.97; H, 8.71.

Other compounds shown in Scheme I were prepared similarly.

***tert*-Butyl Benzoate (**3a**):** 78% yield; bp  $44^\circ\text{C}$  (0.03 Torr);  $n_D^{25}$  1.4886 (lit.<sup>10</sup>  $n_D^{25}$  1.4896).

**Triarylcarbinol **4a**.** From 0.02 mol of **1a** and 1 molar equiv of *n*-BuLi, benzophenone (0.025 mol) in dry THF (30 ml) was added at  $-100^\circ\text{C}$ . The crude product (9.20 g) was recrystallized from petroleum ether (bp  $60\text{--}90^\circ\text{C}$ ) to give a 76% yield of **4a** [mp  $115\text{--}116^\circ\text{C}$ ; NMR ( $\text{CDCl}_3$ )  $\delta$  1.60 (s, 9,  $\text{CH}_3$ ), 3.25 (s, 1, OH), 7.30 (s, 10, ArH), 7.35 (d, 2, ArH), 7.92 (d, 2, ArH)].

Anal. Calcd for  $\text{C}_{24}\text{H}_{24}\text{O}_3$ : C, 79.97; H, 6.71. Found: C, 80.25; H, 6.48.

***p*-Carbo-*tert*-butoxy-*N*-phenylbenzamide (**6a**).** From 0.02 mol of **1a** and 1 molar equiv of *n*-BuLi, phenyl isocyanate (0.02 mol) in dry THF (~15 ml) was added at  $-95^\circ\text{C}$ . The crude solid (6.10 g, mp

121–131 °C) was recrystallized from a mixture (80/20) of petroleum ether (bp 90–110 °C) and chloroform to give a 54% yield of **6a** [mp 147–148 °C; NMR (CDCl<sub>3</sub>) δ 1.60 (s, 9, CH<sub>3</sub>), 7.50 (m, 5, ArH), 7.90 (m, 4, ArH), 8.45 (broad s, 1, NH)].

Anal. Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>: C, 72.71; H, 6.44; N, 4.71. Found: C, 72.93; H, 6.52; N, 4.53.

**Reactions of Isopropyl *p*-Bromobenzoate (1b).** Reactions with isopropyl *p*-bromobenzoate [bp 80 °C (0.03 Torr), 86% yield from *p*-bromobenzoyl chloride and 2-propanol; composition analysis in agreement with C<sub>10</sub>H<sub>14</sub>BrO<sub>2</sub>; NMR (CDCl<sub>3</sub>) δ 1.45 (d, 6, CH<sub>3</sub>), 5.40 (m, 1, CH), 7.50 (m, 3, ArH), 8.15 (m, 2, ArH)] were carried out as described for **1a**. Aliquots taken after 5 min showed considerable amounts of condensation products. The mixture was stirred for a total of 50 min at –105 °C and then poured into water. The organic product obtained from the dried (MgSO<sub>4</sub>) ether extracts showed at least seven components by TLC. A portion (500 mg) of the product was purified by preparative TLC [silica gel, fluorescent indicator, petroleum ether (bp 30–60 °C) and ether mixture (90/10) as eluent] to give in order of decreasing *R<sub>f</sub>* (1) isopropyl benzoate [9% yield; NMR (CDCl<sub>3</sub>) δ 1.45 (d, 6, CH<sub>3</sub>), 5.40 (m, 1, CH), 7.50 (m, 3, ArH), 8.15 (m, 2, ArH)]; (2) isopropyl *p*-bromobenzoylbenzoate [26% yield, mp 82–83 °C from petroleum ether (bp 60–90 °C); NMR (CDCl<sub>3</sub>) δ 1.45 (d, 6, CH<sub>3</sub>), 5.38 (m, 1, CH), 7.71 (s, 4, ArH), 7.85 (d, 2, ArH), 8.1 (d, 2, ArH) (Anal. Calcd for C<sub>17</sub>H<sub>15</sub>BrO<sub>3</sub>: C, 58.81; H, 4.85; Br, 23.02. Found: C, 58.77; H, 4.42; Br, 23.16)]; (3) an oil, slightly impure alcohol corresponding to the product obtained by addition of *n*-butyllithium to isopropyl *p*-bromobenzoylbenzoate [19% yield; NMR (CDCl<sub>3</sub>) δ 0.9 (t, 3, CH<sub>3</sub>), 1.40 (d, ~6, CH<sub>3</sub>), 1.40 (m, ~6, CH<sub>2</sub>), 5.35 (m, 1, CH), 7.55 (m, 6, ArH), 8.10 (d, 2, ArH); ir (CCl<sub>4</sub>) ν<sub>OH</sub> 3440 cm<sup>-1</sup>, ν<sub>C=O</sub> 1710 cm<sup>-1</sup>]; and (4) the major fraction, with low *R<sub>f</sub>*, which was a complex mixture.

**Reactions of Isopropyl *o*-Bromobenzoate (7).** Isopropyl *o*-bromobenzoate [7, 83% yield from *o*-bromobenzoyl chloride and 2-propanol, bp 86–87 °C (0.01 Torr); NMR (CDCl<sub>3</sub>) δ 1.38 (d, 6, CH<sub>3</sub>), 5.13 (m, 1, CH), 7.43 (m, 4, ArH) (Anal. Calcd for C<sub>10</sub>H<sub>11</sub>BrO<sub>2</sub>: C, 49.41; H, 4.56; Br, 32.87. Found: C, 49.18; H, 4.58; Br, 32.76)] was treated with *n*-BuLi as described for **1a**. Studies (NMR) of aliquots taken after 5 min showed absence of starting bromo ester and only isopropyl benzoate.

**Lactone 9.** To the solution prepared from bromo ester **7** (0.0206 mol) and *n*-BuLi stirred for 20 min at –105 °C was added cyclohexanone (0.03 mol) in dry THF (~25 ml) at –100 °C. The resulting solution was allowed to warm to 10 °C and was poured into dilute hydrochloric acid (~100 ml). The acidic solution was extracted with ether and the organic material obtained from the dried (MgSO<sub>4</sub>) ether extracts was saponified (1.5 h) with hot 90% ethanolic KOH. The solution was cooled and extracted with ether (the ether extract contained 1.39 g of an oil which was resaponified and reprocessed to give 0.34 g, 9% yield, of lactone **9**). The alkaline mixture was made acidic (pH ~2) with concentrated hydrochloric acid and warmed at 50 °C

for 5 min. The cooled solution was extracted with ether, which was subsequently washed rapidly with cold 5% aqueous NaOH. Lactone **9** (1.35 g, 34% yield, total yield 43%, mp and mmp<sup>5</sup> 79–80 °C) was obtained from the dried (MgSO<sub>4</sub>) ether extract by recrystallization of the crude product from petroleum ether (bp 30–60 °C).

***N*-Phenylphthalimide (10).** Phenyl isocyanate (0.05 mol) in dry THF (~25 ml) was added at –98 °C to the solution prepared from isopropyl *o*-bromobenzoate (0.020 mol) 5 min after the addition of *n*-BuLi. The mixture was allowed to warm to 25 °C and was poured into water (~100 ml). Phthalimide **10** (mp 208–210 °C, from ethanol/chloroform, mmp 206–209 °C, lit.<sup>11</sup> mp 208 °C) was obtained in 53% yield by recrystallization of the solid mixture obtained from the dried (MgSO<sub>4</sub>) organic extracts. The concentrated mother liquor contained *N,N'*-diphenylurea (mp 237–242 °C dec, lit.<sup>12</sup> 239 °C, separated by trituration with petroleum ether in which the urea has limited solubility) and a product assumed to be slightly impure isopropyl *N*-phenylcarbamate [mp 85–86 °C, by preparative TLC with subsequent recrystallization from petroleum ether (bp 30–60 °C); lit.<sup>13</sup> mp 86 °C; NMR (CDCl<sub>3</sub>) δ 1.30 (d, 6, CH<sub>3</sub>), 5.05 (m, 1, CH), 6.6 (broad s, 1, NH), 7.20 (m, 5, ArH); ir (KBr) ν<sub>N-H</sub> 3300 cm<sup>-1</sup>, ν<sub>C=O</sub> 1710 cm<sup>-1</sup>].

Anal. Calcd for C<sub>10</sub>H<sub>13</sub>NO<sub>2</sub>: C, 67.02; H, 7.82; N, 7.82. Found: C, 67.56; H, 7.24; N, 7.82.

**Registry No.**—**1a**, 59247-47-1; **1b**, 59247-48-2; **3a**, 774-65-2; **4a**, 59247-49-3; **5a**, 59247-50-6; **6a**, 59247-51-7; **7**, 59247-52-8; **9**, 5651-49-0; **10**, 520-03-6; *n*-butyllithium, 109-72-8; cyclohexanone, 108-94-1; benzophenone, 119-61-9; phenyl isocyanate, 103-71-9; *p*-bromobenzoyl chloride 586-75-4; 2-propanol, 67-63-0; isopropyl benzoate, 939-48-0; *o*-bromobenzoyl chloride, 7154-66-7; isopropyl *n*-phenylcarbamate, 122-42-9; isopropyl *p*-bromobenzoylbenzoate, 59247-53-9.

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## Metal-Ammonia Reduction. 15. Regioselectivity of Reduction and Reductive Methylation in the Fluorene Series<sup>1</sup>

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Reduction of fluorene with alkali metals in ammonia affords initially 2,4a-dihydro- and 1,4-dihydrofluorene (**2**, **3**) and not the 3,9a isomer previously reported. While **2** accords with molecular orbital prediction, **3** is only the second example of reduction contratheory. Analogous reductive methylation of fluorene with lithium and methyl bromide gave the 4a-methyl homologue of **2**, 4a-methyl-2,4a-dihydrofluorene, along with 9-methyl- and 9,9-dimethylfluorene. The products of similar reactions of 9,9-dimethylfluorene were principally the predicted 2,4a-dihydro derivatives accompanied by lesser amounts of the 1,4-dihydro isomers, namely 1,4-dihydro-9,9-dimethylfluorene and its 1-methyl homologue. Formation of the 2,4a-dihydro products is explicable in terms of the general mechanism previously proposed, while origin of the 1,4-dihydro compounds involves initial protonation unexpectedly at the 4 position. Formation of the 9-methylated derivatives of fluorene is ascribed to protonation by fluorene of the dianionic intermediate and methylation of the 9-fluorenyl anion.

Reduction of polycyclic aromatic hydrocarbons by alkali metals in liquid ammonia has been shown in previous pa-

pers<sup>1,3,4</sup> to be controllable to the dihydro stage, to be regioselective,<sup>5</sup> and to afford products in accord with predictions of