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Publisher Taylor & Francis

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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Mogi, Kaori, Takenaka, Keiko and Okazaki, Renji(2005) 'Thiophilic Reactions of Aryllithium Bearing a Bulky Bowl-Type Substituent With Carbon Disulfide', Phosphorus, Sulfur, and Silicon and the Related Elements, 180: 5, 1501 — 1502

To link to this Article: DOI: 10.1080/10426500590913384

URL: <http://dx.doi.org/10.1080/10426500590913384>

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Thiophilic Reactions of Aryllithium Bearing a Bulky Bowl-Type Substituent With Carbon Disulfide

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Reactions of aryllithium that have a bulky bowl-type substituent, Bmt (Bmt = 4-*t*-butyl-2,6-bis[2,2'',6,6''-tetramethyl]phenyl) with carbon disulfide, afforded various compounds *via* interesting anion intermediate **1**, resulting from a thiophilic attack of the lithium reagent.

BmtLi reacted with carbon disulfide to give alkene **cis-3** (R=CH₃) after treatment with methyl iodide. **cis-3** (R=CH₃) isomerized to thermodynamically more stable **trans-3** (R=CH₃) upon heating or treatment with acid. The formation of **cis-3** (R=CH₃) can be explained in terms of reaction of dianion **2**, which is formed by dimerization of anion **1**, which has dithiocarbene-type canonical structure **1b**, with methyl iodide. The use of *p*-methylbenzyl bromide instead of methyl iodide gave **trans-3** (R=CH₂C₆H₄CH₃-*p*). We also examined more bulky alkyl halides, MesCH₂Br and TipCH₂Br (Tip = 2,4,6-tri-isopropylphenyl). These alkyl halides did not react with **2** but with monomeric anion **1a** to afford the corresponding dithioester **4**. This suggests the existence of a monomer **1**–dimer **2** equilibrium. Reaction with a sterically more congested alkyl halide, Mes^{*}CH₂Br (Mes^{*} = 2,4,6-tri-*t*-butylphenyl), resulted in the formation of **5**. This clearly shows the elimination of carbon monosulfide from **1**. This elimination occurs most likely because Mes^{*} group is so sterically congested that even **1** could not react with this bromide at low temperature. The even more bulky alkyl halide, TmtCH₂Br (Tmt = 2,2'',6,6''-tetramethyl-*m*-terphenyl) did not react with **6**, and only thiol BmtSH was obtained. Interestingly, use of protic acid such as trifluoromethanesulfonic acid and aq. HCl as a quenching reagent

Received July 9, 2004; accepted October 5, 2004.

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resulted in unexpected formation of dithioformate **7**. The mechanism for the formation of these products is discussed.

Structures of **3**, **4**, **5** and **7** were established by X-ray crystallographic analysis.

