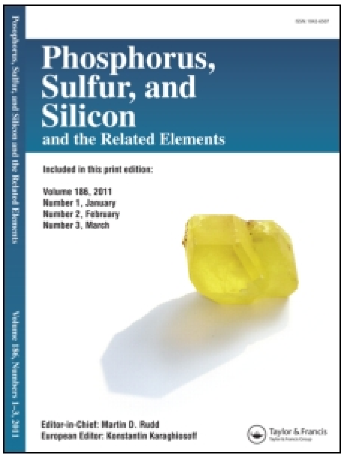

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Thiophilic Reactions of Aryllithium Bearing a Bulky Bowl-Type Substituent With Carbon Disulfide

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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″-tetramathyl]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=CH_3) after treatment with methyl iodide. ***cis*-3** (R=CH_3) isomerized to thermodynamically more stable ***trans*-3** (R=CH_3) upon heating or treatment with acid. The formation of ***cis*-3** (R=CH_3) 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=$CH_2C_6H_4CH_3$-*p*). We also examined more bulky alkyl halides, $MesCH_2Br$ and $TipCH_2Br$ (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*CH_2Br (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, $TmtCH_2Br$ (Tmt = 2,2″,6,6″-tetramathyl-*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

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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.