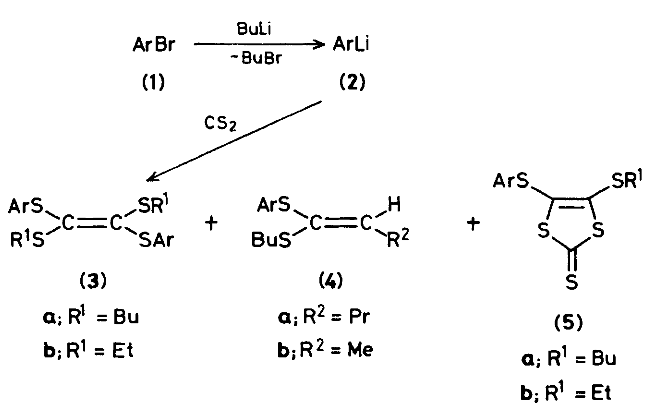
Thiophilic Reaction of 2,4,6-Tri-t-butylphenyl-lithium with Carbon Disulphide: Umpolung of the Reactivity of Carbon Disulphide

Renji Okazaki,* Takuji Fujii, and Naoki Inamoto
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

The first example of thiophilic attack of an organolithium reagent on carbon disulphide is described.

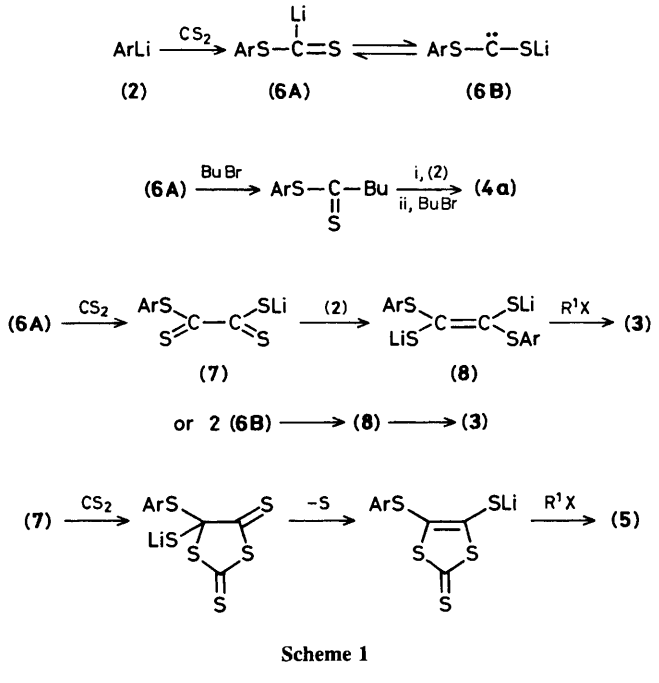
The reaction of thiocarbonyl compounds with organometallic reagents has attracted much attention in recent years because it is quite different from that of carbonyl compounds: Grignard and organolithium reagents undergo *C*-addition, *S*-addition (thiophilic reaction), or *C,S*-double addition depending on the nature of the thiocarbonyl compound and the organometallic reagent.[1,2]

We report here the first example of a thiophilic reaction of an organolithium reagent with carbon disulphide. The reaction of 2,4,6-tri-t-butylphenyl-lithium (**2**), generated from 2,4,6-tri-t-butylbromobenzene (**1**) and butyl-lithium (1.2 equiv.) at −78 °C, with carbon disulphide (1.2 equiv.) at the same temperature in tetrahydrofuran afforded compounds (**3a**) (41%), (**4a**) (19%), and (**5a**) (4%).† In order to avoid the involvement of butyl bromide in the reaction, compound (**2**) was prepared from (**1**) and t-butyl-lithium (2 equiv.) and allowed to react at −78 °C with carbon disulphide (2.7 equiv.) and then, after 2 h, with ethyl iodide (2 equiv.). In this case the products were (**3b**) (59%) and (**5b**) (19%), no (**4b**) being formed.†



The formation of compounds (**3**)—(**5**) may be accounted for by the mechanism in Scheme 1, beginning with the attack of (**2**) on the sulphur atom of carbon disulphide. The alkene (**3**) is formed by the reaction of the carbanion (**6A**) with carbon disulphide followed by reaction with (**2**) or by the dimerization of the dithiocarbene (**6B**). The formation of (**5**) is explicable in terms of the reaction of (**6**) with two molecules of carbon disulphide followed by loss of sulphur. This reaction is somewhat similar to the formation of 1,3-dithiole-2-thione derivatives from alkali metal or electrolytic reduction of carbon disulphide.[3]

The reaction of Grignard and organolithium reagents with carbon disulphide is an important method for the synthesis of dithiocarboxylic acid derivatives and many examples are known,[1,4,5] but we are unaware of any precedent in which the sulphur atom of carbon disulphide is attacked. The present



Scheme 1

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† The products (**3**)—(**5**) were identified by spectral (^{1}H and ^{13}C n.m.r.; mass) and analytical data (elemental and/or exact mass). For (**3a**), (**3b**), and (**4a**) only a single isomer was obtained which was tentatively assigned the stereochemistry indicated for steric reasons.

results suggest that umpolung of the reactivity of carbon disulphide [*i.e.*, the formation of the carbanion $RSC(=S)^-$]‡ can be achieved by using a very sterically hindered lithium reagent although further elaboration of the reaction conditions is necessary for synthetic application.

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‡ The formation of a similar carbanion, $R_2NC(=S)^-$, from thioformamides and a strong base and its synthetic application have been reported.[6]