

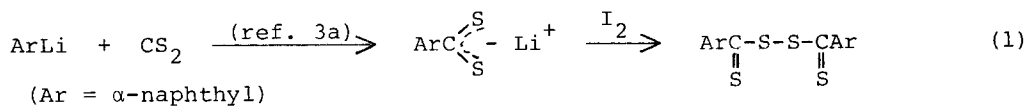
Reactions of In-Situ Generated Acyllithium Reagents with Carbon Disulfide and Carbonyl Sulfide.

Dietmar Seyferth* and Richard C. Hui

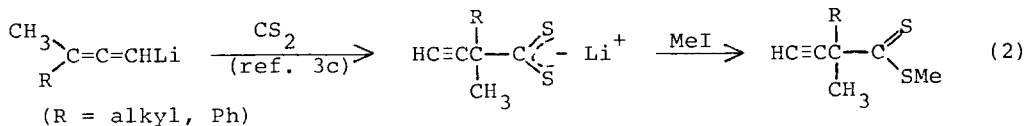
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139 (U.S.A.)

Summary. In-situ generated (at -110°C to -135°C) acyllithium reagents, RC(O)Li (R = *t*-Bu, *n*-Bu), react with CS₂ to give [RCOS]Li with loss of CS. On the other hand, COS reacts to give [RC(O)COS]Li.

Like alkyl- and aryllithium reagents, in-situ generated acyllithium reagents¹ cleave the S-S bond of disulfides, RSSR, and react with elemental sulfur.² Organolithium reagents also react with carbon disulfide³ (e.g., eq.1 and



eq.2). It was of interest to see if acyllithium reagents would undergo similar



reactions with CS₂ to give, after alkylation of the intermediate lithium dithiocarboxylate, novel products of type RC(O)CS₂R'.⁴

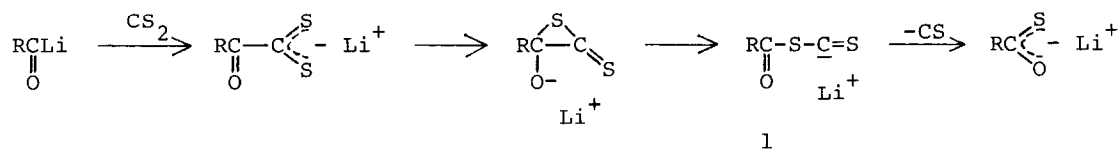
We have examined the reactions of the *t*-BuLi/CO and *n*-BuLi/CO reagents (generated in situ at very low temperature) with carbon disulfide. In a typical experiment, a 500 ml three-necked flask equipped with a stirrer, a Claisen adapter (fitted with a low temperature thermometer and a gas outlet tube) and a no-air stopper which held a gas dispersion tube (which was connected to a carbon

monoxide cylinder) was charged with 300 ml of a 4:4:1 THF/Et₂O/pentane mixture and 0.697 g (9.14 mmol) of CS₂ (distilled from P₂O₅). This solution was cooled to -110°C and CO was bubbled in for 30 min. Then, while the CO stream was continued, a solution of *t*-butyllithium (2.40N in pentane, 3.8 ml, 9.12 mmol) was added at a rate of 0.24 ml/min by means of a syringe pump (Orion Research, Inc., Model 341). After the addition had been completed, the now reddish-brown reaction mixture was stirred under CO at -110°C for 2h and subsequently was allowed to warm to -50°C (still under CO). Iodomethane (1.3 ml, 20.9 mmol) was added; no color change was observed. The mixture was allowed to warm to room temperature and then was treated with 50 ml of distilled water. The organic layer and ether washings of the aqueous layer were dried and concentrated. GLC analysis of the residue showed the presence of a single product, the known² *t*-BuC(O)SCH₃ in 58% yield. The residue was trap-to-trap distilled (22°C at 0.8 mmHg). The IR and NMR spectra of the distillate confirmed the presence of *t*-BuC(O)SCH₃; thus the apparent loss of CS was not an artifact of GLC analysis). A similar reaction of the *n*-BuLi/CO reagent, generated in the presence of an excess of CS₂ at -135°C using the procedure described above, gave *n*-BuC(O)SCH₃ (after CH₃I quench) in 54% yield.

The formation of S-methyl thioesters in these reactions implies that a lithium thiocarboxylate, [RCOS]Li, is present in solution when CH₃I is added. With this in mind, two such *t*-BuLi/CO/CS₂ reaction mixtures (-110°C reaction temperature) were quenched with trimethylchlorosilane and trimethyltin bromide, respectively. In the case of the Me₃SiCl quench, *t*-BuC(S)OSiMe₃ was obtained in 64% yield.⁵ With Me₃SnBr the product (62% yield) was *t*-BuC(O)SSnMe₃.⁶ This is an interesting case of an O,S ambident anion reaction where the well-known oxophilicity of silicon and the thiophilicity of tin are the product-determining factors.

We suggest that in the case of the reactions of acyllithiums with CS₂ the nucleophilic attack occurs at carbon (as with RLi and ArLi), with subsequent extrusion of CS to give the lithium monothiocarboxylate (Scheme 1). (The reddish-brown color of the reaction mixture could possibly be due to the formation of

CS polymers.) A second possibility is direct thiophilic attack (of the type known for the reactions of PhLi with Ph₂C=S, PhCS₂Ph and (PhS)₂C=S⁷) of the acyllithium on CS₂ to form intermediate 1 directly. However, we prefer the reaction course shown in Scheme 1 on the basis of results obtained with COS.



SCHEME 1

One might expect the acylcarboxylate anion formed by attack of RC(O)Li on carbonyl sulfide, [RC(O)COS]Li, to be more stable than [RC(O)CS₂]Li and this is indeed the case. In such a reaction, 8.56 mmol of *t*-BuLi in pentane was added as described above to a CO-saturated solution of ~8.7 mmol of COS (Matheson) in 4:4:1 THF/Et₂O/pentane at -110°C and the reaction mixture subsequently was quenched with 21 mmol of CH₃I. The product, which was obtained in 68% yield, was a yellow liquid, n²⁰_D 1.4679, which was identified as the acyl thioester, *t*-BuC(O)C(O)SCH₃.⁸

This and our previous report² have demonstrated that our new acyllithium methodology is usefully applicable in organosulfur synthesis. Our development of the applications of in situ acyllithium chemistry is continuing.

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References and Notes.

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 5. A light yellow liquid, n_D^{20} 1.4449; lit. n_D^{20} 1.4440 [H.R. Kricheldorf and E. Leppert, Synthesis, 435 (1971)]. In the IR spectrum no $\nu(\text{C=O})$ is apparent.
 6. A colorless liquid, n_D^{20} 1.5017; $\nu(\text{C=O})$ 1648 cm^{-1} ; satisfactory C,H,S analysis.
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