

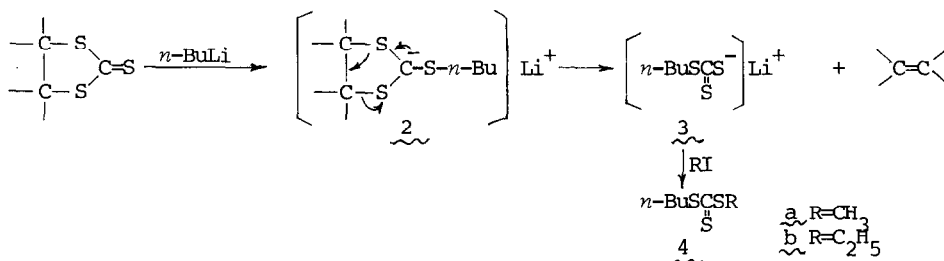
THE REACTION OF FIVE-MEMBERED CYCLIC TRITHIOCARBONATES WITH *n*-BUTYLLITHIUM

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Summary: It was found that the reaction of five-membered cyclic trithiocarbonates with *n*-butyllithium in tetrahydrofuran is applicable to the preparation of unsymmetrical linear trithiocarbonates and further to the interconversion of *cis*- and *trans*-olefins.

Five-membered cyclic trithiocarbonates have been shown to be in general readily accessible and synthetically useful compounds.¹⁻⁵ In this letter, we wish to report our findings concerning reactions of the trithiocarbonates with *n*-butyllithium (*n*-BuLi) in tetrahydrofuran. When the reaction of 1,3-dithiolan-2-thione 1, which is the simplest member of the above-mentioned trithiocarbonates, with *n*-BuLi in tetrahydrofuran was quenched with methyl and ethyl iodides, *n*-butyl methyl trithiocarbonate 4a and *n*-butyl ethyl trithiocarbonate 4b⁶ were obtained (77 and 72% yield, respectively). It seems reasonable that the reaction involves direct attack¹ of the nucleophile on the sulfur of the thiocarbonyl leading to an intermediate anion 2 and subsequent fragmentation of 2 to an olefin and *n*-butyl trithiocarbonate anion 3.



Although we have only investigated the reactions with methyl and ethyl iodides as the alkylating agent, it is clear that the 1,3-dithiolan-2-thione route is of considerable potential and can furnish an alternative means of preparation of unsymmetrical linear trithiocarbonates.⁶⁻⁸

More important from the synthetic point of view is the discovery that this constitutes, together with the reaction proposed by Overberger and Drucker,³ a new process of the interconversion of *cis*- and *trans*-olefins. For example, *cis*- and *trans*-stilbene are converted to *trans*-4,5-diphenyl-1,3-dithiolan-2-thione 5 and its *cis*-isomer 6, respectively. Thus, the compound 5 was reacted with *n*-BuLi in tetrahydrofuran at -78°C to afford *trans*-stilbene in 100% yield. Similarly, *cis*-stilbene was obtained free of isomeric impurity in 99% yield from 6. Treatment of *trans*-1,2-cyclooctene trithiocarbonate 7, which is easily accessible from *cis*-cyclooctene, with *n*-BuLi in tetrahydrofuran at -78°C for 2 hr afforded *trans*-cyclooctene

of > 98% purity in 39% yield. The elimination reaction of these cyclic trithiocarbonates has been performed by heating at reflux with triethyl phosphite for 24-50 hr.² In contrast, the reaction with *n*-BuLi proceeds rapidly at low temperature, and hence would be utilized for the preparation of an olefin which is sensitive to elevated temperatures.

Synthesis of 4: To a solution of 1 (1.36 g, 10 mmol) in tetrahydrofuran (10 ml) at -78°C was added a 1.56 molar solution (7.7 ml, 12 mmol) of *n*-BuLi in hexane under nitrogen. After 30 min, methyl iodide (or ethyl iodide) (12 mmol) was added and the mixture was stirred for 3 hr at -78°C. It was poured into a large quantity of cold brine and extracted with several portions of ether. The combined ethereal extracts were dried and the solvent was removed to give the residual products. Column chromatographies were performed on silica gel.

Conversion of *trans*-stilbene to *cis*-stilbene: The intermediate trithiocarbonate 6 was prepared from *trans*-stilbene by the procedure cited.³ To a solution of 6 (0.288 g, 1 mmol) in tetrahydrofuran (2 ml) at -78°C was added a 1.56 molar solution (0.71 ml, 1.1 mmol) of *n*-BuLi in hexane under nitrogen. The mixture was stirred for 45 min at -78°C protected from daylight and worked up as above. *trans*-Stilbene was also formed by the similar procedure from *cis*-stilbene.

Synthesis of *trans*-cyclooctene: The reaction of 7 (1.03 g, 4.71 mmol) in tetrahydrofuran (5 ml) with a 1.56 molar solution (6.6 ml, 10.3 mmol) of *n*-BuLi in hexane under the similar conditions, except for reaction time (2 hr), provided *trans*-cyclooctene. The yield was determined by gas chromatographic analysis.

The present findings offer the possibilities for the preparation of unsymmetrical linear trithiocarbonates and further for the easy interconversion of *cis*- and *trans*-olefins.

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