CONVERSION OF FIVE-MEMBERED CYCLIC TRITHIOCARBONATES TO ALKYL VINYL TRITHIOCARBONATES WITH LITHIUM DIISOPROPYLAMIDE

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Summary: Alkyl vinyl trithiocarbonates could be prepared by deprotonation of five-membered cyclic trithiocarbonates with lithium diisopropylamide in tetrahydrofuran followed by treatment with alkylating agent.

There has been recent interest in the reactions of five-membered cyclic trithiocarbonates.¹⁻³ In this communication we report that a variety of alkyl vinyl trithiocarbonates can be prepared in synthetically useful yields by reaction of the above-mentioned cyclic trithiocarbonates with lithium diisopropylamide in tetrahydrofuran followed by treatment with the appropriate alkylating agent. For example, 1,3-dithiolan-2-thione 1 was readily converted into alkyl vinyl trithiocarbonates with the formula of 5 in yields of 42-87% (see Table 1).

 $\begin{array}{ccc} \text{CH}_2 = \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{CH}_3 & \underset{\text{CH}_2}{\overset{\text{CH}_2 + 1}{\overset{\text{CH}_2 + 1}{\overset{CH}_2 + 1}{\overset{CH}_2 + 1}{\overset{CH}_2 + 1}{\overset{CH}_2 \\{CH}_2 + 1}{\overset{$

Apparently the reaction proceeds by deprotonation to give a species such as $\underline{6}$, which undergoes electron transfer leading to vinyl trithiocarbonate anion 7. The anion 7 thus formed is subsequently alkylated by the alkyl halides to produce predominantly the corresponding alkyl vinyl trithiocarbonates. It is in an interesting contrast with the reaction of $\underline{1}$ with *n*-BuLi which involves initial attack of the *n*-butyl anion on the sulfur of the thiocarbonyl in $\underline{1}$.

$$s=c_{S-C-}^{S-C-} \xrightarrow{[(CH_3)_2CH]NLi} \left(s=c_{S-C}^{S-C_1}\right) \xrightarrow{RX} \xrightarrow{RSCSS} c_{S-C}^{C_1}$$

It has been found that the present procedure is also applicable to 4-methyl-2, 4-phenyl-3 and *cis*-4,5-diphenyl-1,3-dithiolan-2-thione 4. As can be seen from Table 1, the deprotonation of 2 to afford its carbanion intermediate 6 occurs only on the carbon atom to which the methyl group is not bonded. Between two methylene protons on the carbon atom, the one *anti* to the methyl group can be removed more easily than *syn*-oriented one. On the other hand, by treatment of 3 with lithium diisopropylamide, both the abstraction of the proton *anti* to the phenyl group and that of the methine proton on the carbon atom, which has the phenyl substituent, competively take place.

The general procedure is as follows: To a stirred solution of diisopropylamine (1.21 g, 12 mmol) in tetrahydrofuran (10 ml) was added at -78°C a 1.56 molar solution (7.7 ml, 12 mmol) of *n*-BuLi in hexane under nitrogen, followed by stirring at the same temperature for 30 min and further at -15°C for 10 min. The solution of lithium diisopropylamide prepared as above

Start mater	ing Alkylating ial agent	Product ^a	Yield(%)
1	CH3I	5a	87
1	C2H5I	<u>5b</u> .	76
1	C ₂ H ₅ Br	<u>5b</u>	46
1	CH ₃ (CH ₂) 2 ^I	5 <u>c</u>	79
1	CH3 (CH2) 2Br	5 <u>5</u> .	56
1	(CH ₃) ₂ CHI	5d	42
Ţ	C6H5CH2Br	<u>5e</u>	83
ŗ	C6H5CH2C1	5e	66
ŗ	CH2=CHCH2Br	廷	82
1	CH2=CHCH2C1	<u>5f</u>	47
2	CH ³ I	CH ₃₂ H	$\approx \begin{cases} cis-15 \\ cis-77 \end{cases}$
2	C6 ^{H5} CH5Br	H SCSSCH ₃ CH ₃₃ H H SCSSCH ₂ C ₆ H ₅	$ \begin{array}{c} $
3~	CH ³ I	$ \begin{pmatrix} C_6 H_{23} & H \\ & C_6 C_{23} & C_{23} \\ & H & SCSSCH_3 \end{pmatrix} $	$ \begin{array}{c} 10\\ \sim\\ trans-37 \end{array} $
		$\begin{bmatrix} CH_2 = C \\ CH_2 = C \\ SCSSCH_3 \\ C_{-}H_{-} \\ C_{-}H_{-} \end{bmatrix}$	11 32
<u>4</u>	CH ₃ I	^{с6-5} с=с ⁷⁶⁻⁵ н SCSSCH ₃	12 47

Table 1. Preparation of Alkyl Vinyl Trithiocarbonates

^aAll the products are new compounds. They showed ir and NMR spectra consistent with the indicated structures and correct combustion analysis ($\frac{1}{2}$ 0.3%) or exact mass measurements by mass spectrometry.

was cooled again to -78° C and a concentrated solution of a five-membered cyclic trithiocarbonate (10 mmol) in tetrahydrofuran was added. After an additional 40 min at -78° C, an alkylating agent (12 mmol) was added carefully and the mixture was stirred for 2 hr at the same temperature (in reaction with less electrophilic alkyl halides, the stirring was performed at -15° C for 12 hr). After removal of the cooling bath, the reaction mixture was poured into 200 ml of brine and extracted with several portions of ether. The combined extracts were dried (MgSO₄), filtered, and concentrated *in vacuo* to give a yellow coloured residue. The product was isolated by column chromatography on silica gel with hexane as the eluent.

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