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THIOPHILIC ADDITION OF ALKYLLITHIUM TO DITHIOCARBOXYLIC ACID ANIONS : SYNTHESIS OF 2-[BIS(ALKYLTHIO)METHYLENE]-1,3-DITHIOLES

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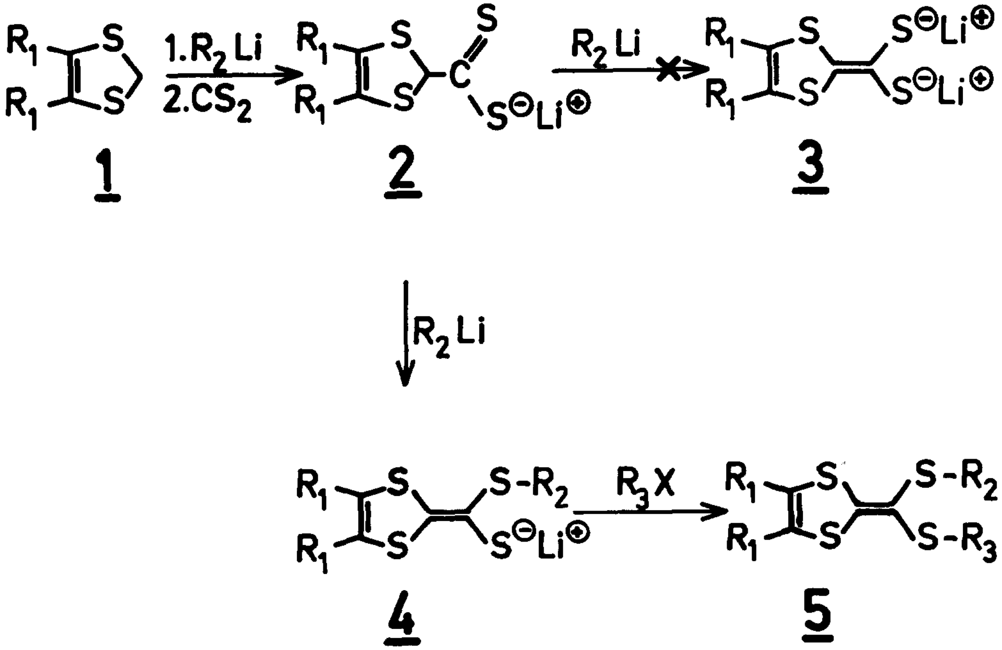
Abstract: 2-lithio-4,5-disubstituted-1,3-dithioles react with CS_2 in the presence of an excess organolithium reagents yielding a product of thiophilic addition; subsequent alkylation furnished a new series of 2-[bis(alkylthio)methylene]-1,3-dithioles.

Organic conductivity and superconductivity is a subject of intense research in recent years.[2] Efforts aimed at developing new electron donors, prompted us to investigate the preparation of dianons of type 3 (scheme) which might be useful as synthons and/or as new redox-active ligands. While 1,3-dithiane anions have received much attention,[3] the analogous "antiaromatic"[4] anions derived from direct metalation of 1,3-dithioles are rare.[5] Moreover, nucleophilic addition of active methylene compounds[6] and of 1,3-dithianes[7] to carbon disulfide is well documented, but similar reactions of 1,3-dithioles are unreported. Our attempts to generate the



dianion 3 from the readily available[8] 1,3-dithioles 1, through metalation and reaction with carbon disulfide, led to unexpected results which we wish to report.

The lithium salt of 4,5-dimethyl-1,3-dithiole 1 which was readily obtained in tetrahydrofuran solution by treatment of the dithiole with 1.1 equiv. of n-butyllithium, reacted spontaneously with carbon disulfide yielding the dithiocarboxylate 2. It was expected that this intermediate will react with a second equiv. of n-butyllithium to yield the dianion 3, which in turn will be methylated (MeI) to form 5(R_1,R_2,R_3=CH_3). Contrary to our expectation following that procedure did not produce the S-methylated compound and the sole isolated product was the butyl, methyl derivative of 5. This experiment clearly showed initial bonding of the carbon of the organolithium reagent to the sulfur of the dithiocarboxylate 2. Addition of R_2Li to 2 and formation of 4 might be rationalized by assuming hydride loss. While H^- is not a usual leaving group, its abstraction from 1,3-dithiole or 1,2-dithiole systems (usually with generation of the aromatic dithiolium salt) was implied in many cases.[9] The anion 4 thus formed, can react with an appropriate electrophile, yielding the tetrathiaethylene derivative 5, and providing access to the hitherto unknown 2-[bis(alkylthio)methylene]-1,3-dithioles.

Similar thiophilic addition have been reported for reactions of organometallics with thioketones,[10] dithioesters,[11] and trithiocarbonates,[11-13] but to the best of our knowledge this is the first example of thiophilic addition to a salt of a dithiocarboxylic acid.

Improved yields of 5 could be obtained by using excess of alkyllithium at the first stage and an equivalent excess of carbon disulfide at the second stage.[14] The following experiment provides details of a typical preparation of 5a. Slow addition of 28 ml of 1.6 *M* *n*-butyllithium in hexane under Ar to 1.32 g (10 mmole) of 4,5-dimethyl-1,3-dithiole 1 in 70 ml. of tetrahydrofuran (-78°C), produced a blue-green solution of the carbanion of 1. To this reagent 3.4 g (45 mmole) of carbon disulfide were added followed by 6.4 g(45 mmole) of methyl iodide. The mixture was stirred for 30 min. and allowed to warm to room temperature. The solvent was evaporated in vacuo, poured into water (75 ml), extracted into ether and dried (Na_2SO_4). The mixture of 5a and methyl butylthiolate were separated by flash chromatography on silica gel with toluene:hexane (1:4) as the eluant. Some of the products obtained as well as their spectral data, are recorded in the Table.

It can be seen that *n*-butyllithium gave best yields, but methyllithium (and probably other organolithium reagents) can add as well. Thus, 2-[bis(methylthio)methylene]-1,3-dithiole(5d) was obtained by using excess methyllithium as the base followed by workup with MeI. That the reac-

Synthesis of 4,5-dimethyl[2- bis(alkylthio)methylene]-1,3-dithioles

compd no	R_2	R_3	yield^a (%)	^{1}H NMR^b	m/z^c
5a	Butyl	Methyl	80	0.91(m,3H), 1.42(m,4H),1.90 (s,6H),2.25(s,3H),2.74(t,2H)	278(37,M)
5b	Butyl	Ethyl	72	0.90(t,3H),1.2(t,3H),1.45 (m,4H),1.88(s,6H),2.72(t+q,4H)^d	292(62,M)
5c	Butyl	Benzyl	77	0.89(t,3H),1.40(s,4H),1.85(s,6H) 2.70(t,2H),3.90(s,2H),7.22(s,5H)	354(35,M)
5d	Methyl	Methyl	46	1.90(s,6H),2.26(s,6H)	236(58,M)
5e	Methyl	CD_3	40	1.90(s,6H),2.26(s,3H)	239(90,M)

a) All yields are of isolated products after flash chromatography and based on starting material 1; b) The number in each entry is the chemical shift value (δ) observed in ppm relative to Me_4Si, followed by the multiplicity of the signal. All spectra were recorded at 90 MHz. Solvent used $CDC\ell_3$; c) Recorded on a NERMAG R10-10 spectrometer; % relative abundance assignment are given; d) Overlapping peaks.

tion with methyllithium occured *via* thiophilic addition to 2, and not through alkylation of the originally aimed dianion 3, was substantiate by working up the reaction with CD_3I and isolating the methyl, trideuteriomethyl derivative 5e.

We are currently studying the scope of this thiophilic reaction and its applicability to other systems. Electrochemical behaviour of compounds 5 and their use as donors, are also under study.[13]

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14. Under these conditions the principal by-product is the alkyldithiolate ($R_2CS_2^-$) isolated as the ester after the alkylation step.
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