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## Formation of $\alpha$ -Allenic Dithioketals in a [2,3] Sigmatropic Rearrangement of Intermediates Derived from S-Propargylic Dithioesters\*

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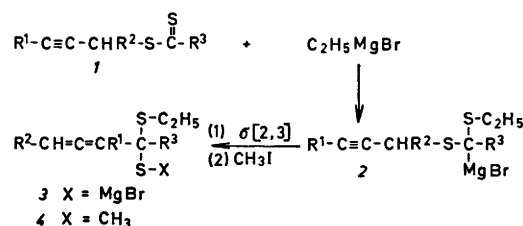
Alkyl Grignard reagents may react with thiocarbonyl compounds, such as thioketones and dithioesters, under thiophilic addition.<sup>1</sup> Recently it was reported<sup>2</sup> that thiophilic addition of Grignard reagents to S-allylic dithioesters is followed by a [2,3] sigmatropic shift of the intermediate carbanion, which gives rise to

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dithioketals of  $\beta$ -unsaturated ketones. Closely related [2,3] sigmatropic rearrangements of  $\alpha$ -metallated allylic thioethers have also been observed.<sup>3</sup>

This communication reports that the thiophilic addition of ethylmagnesium bromide to the double bond of the thiocarbonyl group of S-propargylic dithioesters in THF at  $-30^\circ\text{C}$  is spontaneously followed by a [2,3] sigmatropic rearrangement of the intermediate carbanion. Subsequent methylation of the so formed allenic thiolate gives  $\alpha$ -allenic dithioketals in 58–74% yield, (see Scheme 1). These dithioketals represent a hitherto unknown type of allenic compound.

*Scheme 1.*  $\alpha$ -Allenic dithioketals 4a–d from the reaction of S-propargylic dithioesters 1a–e with ethylmagnesium bromide.



Compound	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	Yield <sup>a</sup> of 4 (%)
1a <sup>5b</sup>	H	H	C <sub>2</sub> H <sub>5</sub>	64
1b <sup>7</sup>	CH <sub>3</sub>	H	C <sub>2</sub> H <sub>5</sub>	69
1c	C <sub>6</sub> H <sub>5</sub>	H	C <sub>2</sub> H <sub>5</sub>	58
1d	CH <sub>3</sub>	H	C <sub>6</sub> H <sub>13</sub>	74
1e	CH <sub>3</sub>	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	—

<sup>a</sup> Isolated by column chromatography.

The allene-forming [2,3] sigmatropic rearrangement in a propargylic system described here is closely related to several analogous reactions known from the literature, especially those in propargylic sulfonium ylides,<sup>4</sup> which afford allenic sulfides.

The propargylic dithioesters 1a–e were prepared according to the literature.<sup>5</sup> A mixture of THF and HMPT was used as the solvent for the alkylation of the alkyldithiomagnesium bromide with the appropriate propargylic bromide. The dithioesters were heat sensitive and could not be distilled at 10 Pa without decomposition but had to be purified by column chromatography.

The thiophilic addition of ethylmagnesium bromide to the thiocarbonyl group of the S-propargylic dithioesters 1a–e is a smooth reaction at  $-30^\circ\text{C}$ . THF is used as the solvent,

as it is known to favour thiophilic addition.<sup>4</sup> The progress of the reaction can be observed by the disappearance of the characteristic yellow colour of the dithioesters. The so formed carbanions *2a-d* rearrange spontaneously through a [2,3] sigmatropic shift and *in situ* methylation of the intermediate *3* by methyl iodide gives the  $\alpha$ -allenic dithioketals *4* in the indicated yields. *In situ* alkylation is used to prevent decomposition of *3* which is otherwise likely to occur.<sup>5</sup> Elimination of ethylthiomagnesium bromide would give an  $\alpha$ -allenic thio-ketone which could react with ethylmagnesium bromide in a second thiophilic addition or could be reduced by the Grignard reagent.

The *S*-propargylic dithioester *1e* obviously reacts with ethylmagnesium bromide in a thiophilic addition, indicated by the discoloration of the reaction mixture, but fails to give an allenic rearrangement product under the above reaction conditions. Reaction of *1e* with isopropylmagnesium bromide, which is known to be more reactive in thiophilic additions,<sup>6</sup> also gave a negative result.

Hydrolysis of the intermediate *3* from a reaction run in the absence of  $\text{CH}_3\text{I}$  gives a variety of products, among which no allenic ketone can be found.

Interestingly, the possibility of a thermal [3,3] sigmatropic rearrangement in *S*-propargylic dithioesters affording *S*-allenyl dithioesters has been pointed out in the literature.<sup>7</sup>

**Experimental.** The general IR and NMR instrumentation has been described.<sup>8</sup> The spectra were routinely recorded and are in full agreement with the proposed structures. Mass spectra were run on an LKB 9000 instrument using the GLC inlet. Correct mass spectral data, run at an ionizing energy of 70 and 15 eV, were obtained for all products.

Preparative column chromatography was performed on silica gel 60 (230–400 mesh), using light petroleum as eluent.

Reactions involving Grignard reagents were performed under nitrogen.

**General procedure for the preparation of dithioesters 1a–e.** Dithioesters *1a–e* were prepared according to Ref. 5. The appropriate Grignard reagent in THF was added dropwise to a solution of  $\text{CS}_2$  in THF at  $-15^\circ\text{C}$ . After stirring for 1 h at this temperature, the alkyl-dithiomagnesium bromide was alkylated with the appropriate propargylic bromide, dissolved in a mixture of THF and HMPT (20% v/v). The reaction mixture was then allowed to reach room temperature during 2 h. The dithioesters were isolated by column chromatography, in the following yields: *1a*<sup>5b</sup> 44%, *1b*<sup>7</sup> 56%, *1c* 53%, *1d* 70% and *1e* 70%.

**Reaction of dithioesters 1a–e with a Grignard reagent.** These reactions were run in analogy with the procedure described in Ref. 2. To 0.045 mol of ethylmagnesium bromide in THF, cooled to  $-30^\circ\text{C}$ , a mixture of 0.045 mol of methyl iodide and 0.015 mol of the dithioester

was added dropwise. The reaction mixture was stirred at this temperature until the characteristic yellow colour of the dithioester had disappeared (1–2 h). Water was then added and the mixture was extracted with ether. The organic phase was washed with saturated  $\text{NH}_4\text{Cl}$  and dried over  $\text{MgSO}_4$ . The allenic products were purified by preparative column chromatography. They have spectroscopic properties characteristic of allenic compounds which are here exemplified for *4a*: IR: 1950 (m), 845 (m, terminal allene)  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ):  $\delta$  1.03 (3 H, t), 1.22 (3 H, t), 1.82 (2 H, q), 2.05 (3 H, s), 2.57 (2 H, q), 4.83–5.50 (3 H, m). MS [IP 15 eV;  $m/e$  (% rel. int.)]: 188 (4, M), 173 (95), 160 (11), 159 (100), 158 (93), 141 (31), 127 (45), 126 (12), 117 (20), 111 (10), 79 (10).

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