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Cleavage of 1,3-Oxathiol-2-one Rings with *n*-Butyllithium A New Route to Alkyl Thiolates

Short Communication

Andrzej Rajca, Damian Grobelny*, and **Stanisław Witek**

Institute of Organic and Polymer Technology, Technical University of Wrocław, PL-50 370 Wrocław, Poland

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1,3-Oxathiol-2-ones are converted by *n*-butyllithium into alkynyl thiolates.

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Spaltung von 1,3-Oxathiazol-2-on-Ringen mit n-Butyllithium. Ein neuer Weg zu Alkylthiolaten (Kurze Mitteilung)

1,3-Oxathiol-2-one werden mit *n*-Butyllithium zu Alkinylthiolaten umgesetzt.

5-Substituted-1,3-oxathiol-2-ones **1**[1], possessing reactive vinyl ester and thioloester functionalities, undergo nucleophilic displacement reactions at the carbonyl carbon with amines[2]. We have found that *n*-butyllithium follows another path of cleavage of the 1,3-oxathiol-2-one ring, which leaves the carbonyl group intact. When 2 moles of *n*-butyllithium in *n*-hexane were added to an anhydrous tetrahydrofuran solution of 1 mole of 5-phenyl-1,3-oxathiol-2-one (**1b**) at —70 °C, and methyl iodide was subsequently added to the yellow reaction mixture, 1-methylthiol-2-phenylethyne (**4d**) (see Table 1) was isolated after common water work up and distillation. Furthermore, valeric acid[3] was obtained with 50% yield from the water layer. The formation of lithium alkynethiolates **3** can be rationalized by the reaction paths as shown in the formula scheme.

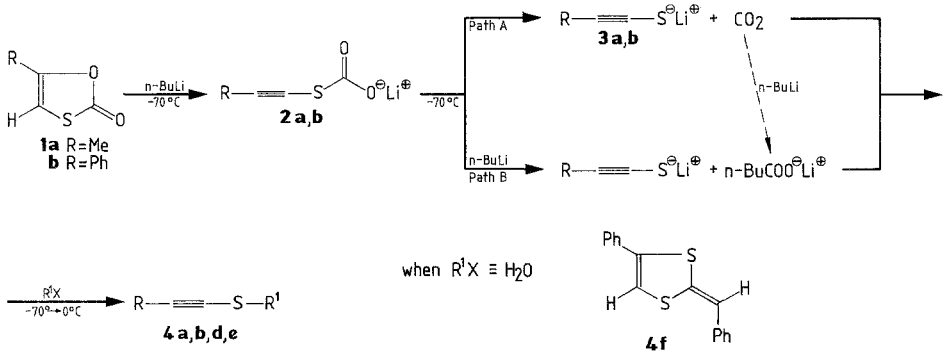
The first step is a nucleophilic eliminative ring fission[4]. The mechanism of cleavage of thiocarbonates **2** is not yet clear. ^{1}H-NMR spectra, however, of the reaction mixtures before distillation show: (i) absence of substrates **1** if 2.0 and even 1.8 moles of *n*-butyllithium were used, (ii) presence of only 25% of the amount of substrate **1b** if an equimolar

Table 1. *1-Alkynyl thioethers* **4a–e**

Compound	*R*	R^1	*X*	Yield[a] [%]	^{1}H-NMR, 60 MHz, TMS, [ppm]	IR [cm^{-1}]
4a	*Me*	*n-Bu*	I	57	(CCl_4): 1.20 (m, 7 H), 1.88 (s, 3 H), 2.53 (t, 2 H)	(neat): — ≡ —, 2210
4b	*Me*	CH_2COOEt	Br	64	(CCl_4): 1.23 (t, 3 H), 1.88 (s, 3 H), 3.27 (s, 2 H), 4.07 (q, 2 H)	(neat): — ≡ —, unrevealed; C=O, 1736
4c[b]	*Me*	CH_2COONa	—	—	(D_2O): 2.23 (s, 3 H), 3.72 (s, 2 H)	(KBr): — ≡ —, 2214; CO_2^-, 1568, 1414
4d	*Ph*	*Me*	I	81	($CDCl_3$): 2.37 (s, 3 H), 7.28 (m, 5 H)	(neat): — ≡ —, 2183
4e	*Ph*	CH_2COOEt	Br	77	($CDCl_3$): 1.22 (t, 3 H), 3.48 (s, 2 H), 4.17 (q, 2 H), 7.28 (m, 5 H)	(neat): — ≡ —, 2185; C=O, 1738

[a] Satisfactory microanalyses obtained with the exception of **4b**.
[b] Obtained by means of hydrolysis of the ethyl ester with methanolic NaOH.

amount of *n*-butyllithium was used. The necessity of less than a 2/1 ratio of *n*-*Bu*Li supports path A, since some carbon dioxide can react with *n*-butyllithium to form the lithium salt of valeric acid. However, path B cannot be completely excluded[5]. If water was carefully added at —70 °C to a tetrahydrofuran/hexane solution of lithium 2-phenylethylenethiolate (**3b**), *trans*-2, *ω*-diphenyl-1,4-dithiafulvene (**4f**) was isolated [53%, m. p. 202–204 °C[6] (chlorobenzene)].



It is notable that deprotonation at the sp^2-hybridized carbon takes preference over nucleophilic attack at the carbonyl group or formation of an allyl lithium derivative. This result is due to the activating effect of sulfur and oxygen on the metallation[7].

In summary, metallation of 1,3-oxathiol-2-ones provides a new method for generation of alkynyl thiolates which represent useful synthetic intermediates[8].

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