A Simple Method for the Preparation of 1,3-Dithiol-2-ones

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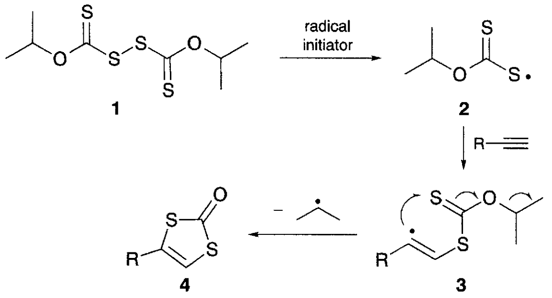
1,3-Dithiol-2-ones are prepared in a single step from diisopropyl xanthogen disulfide and alkyne.

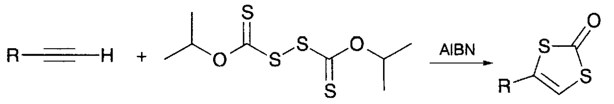
1,3-Dithiol-2-ones (**4**) are direct precursors of tetrathiafulvalenes that are extensively used in conjunction with tetracyano-*p*-quinodimethane (TCNQ) as organic conductors possessing unusually high electrical conductivity.[1] They are also encountered in certain cephalosporins.[2] Methods of preparation of these 1,3-dithiol-2-ones usually require several steps from commercially available starting materials. The last step is generally an intramolecular cyclization either from ketoxanthate[3] or from alkynyl xanthogen derivatives,[4] or from carbon disulfide addition onto an alkynylthiolate.[5]

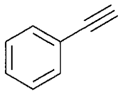
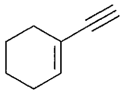
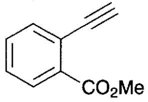
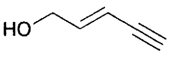
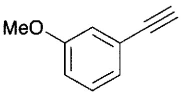
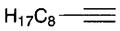
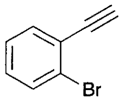
This communication describes a new method for the formation of 1,3-dithiol-2-ones in only one step from commercially available reagents. The first reagent used is an alkyne and acts as a substrate. The second, diisopropyl xanthogen disulfide[†] **1**, contains a masked 1,3-dithiol-2-one functionality that adds to the triple bond of the substrate.



Scheme 1

Table 1 Yields of 1,3-Dithiol-2-ones from terminal alkynes



Alkyne	Yield (%)	Alkyne	Yield (%)
	80		76
	81		82
	78		55[a]
	59		

[a] Yield based on recovered starting material.

We envisioned that under radical conditions the disulfide bond of **1** is expected to cleave to form the thiyl radical **2**, which in presence of the alkyne could add at the C-terminal[6] and form a vinyl radical **3**. This radical, being well-positioned for a 5-*exo-trig* cyclization on the carbon–sulfur double bond, could yield the carbonyl bond of the 1,3-dithiol-2-one **4** by extruding an isopropyl radical (Scheme 1).

Indeed, when a benzene solution of phenylacetylene was heated at 80 °C with diisopropyl xanthogen disulfide and AIBN (50%) a good yield of 4-phenyl-1,3-dithiol-2-one was isolated after chromatography (Table 1). The physical data (mp, ^1H NMR) of the 4-phenyl-1,3-dithiol-2-ones thus obtained are in accordance with the reported values.[3][‡] When less than 1 equiv. of xanthogen was used, a much lower yield was obtained. These reaction conditions are mild and tolerated for many functional groups such as methoxy, ester and even bromine, which is well known to react in a radical processes.

We are presently evaluating the scope and limitation of this reaction with other functionalities and the results will be published elsewhere.

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Footnotes

[†] Available from Pfaltz and Bauer Inc.

[‡] Mp 95–96° C; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.81 (1H, s) and 7.40 (5H, m); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 111.8, 126.5, 129.4, 132.8, 135.1 and 192.7; Anal. calc. for $C_9H_6OS_2$: C, 55.64; H, 3.11; S, 33.01. Found: C, 55.68; H, 3.13; S 33.25%.

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