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

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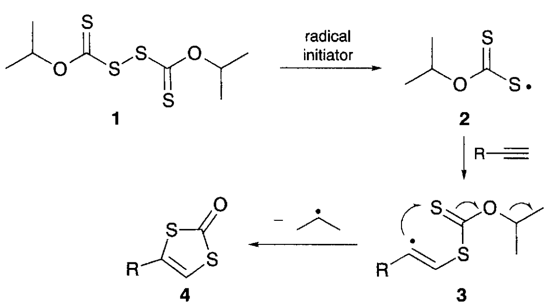
1,3-Dithiol-2-ones are prepared in a single step from diisopropyl xanthogen disulfide and alkyne.

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

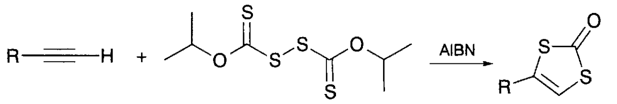
We envisioned that under radical conditions the disulfide bond of **1** is expected to cleave to form the thiyl radical **2**, which in presence of the alkyne could add at the C-terminal[6] and form a vinyl radical **3**. This radical, being well-positioned for a 5-*exo-trig* cyclization on the carbon–sulfur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

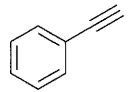
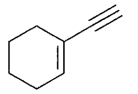
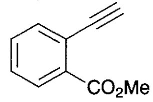
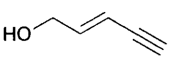
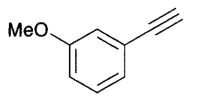
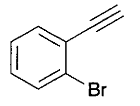
Indeed, when a benzene solution of phenylacetylene was heated at 80 °C with diisopropyl xanthogen disulfide and AIBN (50%) a good yield of 4-phenyl-1,3-dithiol-2-one was isolated after chromatography (Table 1). The physical data (mp, ^{1}H NMR) of the 4-phenyl-1,3-dithiol-2-ones thus obtained are in 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.

The author wishes to thank Dr S. Z. Zard for useful suggestions.

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



Alkyne	Yield (%)	Alkyne	Yield (%)
	80		76
	81		82
	78	$H_{17}C_8$—≡	55^a
	59		

^{a} Yield based on recovered starting material.

Received, 6th March 1995; Com. 5/01344E

Footnotes

[†] Available from Pfaltz and Bauer Inc.

[‡] Mp 95–96° C; ^{1}H 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%.

References

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