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## Simple Method for the Preparation of 1,3-Dithiol-2-one and 1,3-Dithiol-2-thione

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**Abstract** The reaction of diisopropyl xanthogen and thio-diisopropyl xanthogen disulfide with alkynes furnished 1,3-dithiol-2-one and 1,3-dithiol-2-thione.

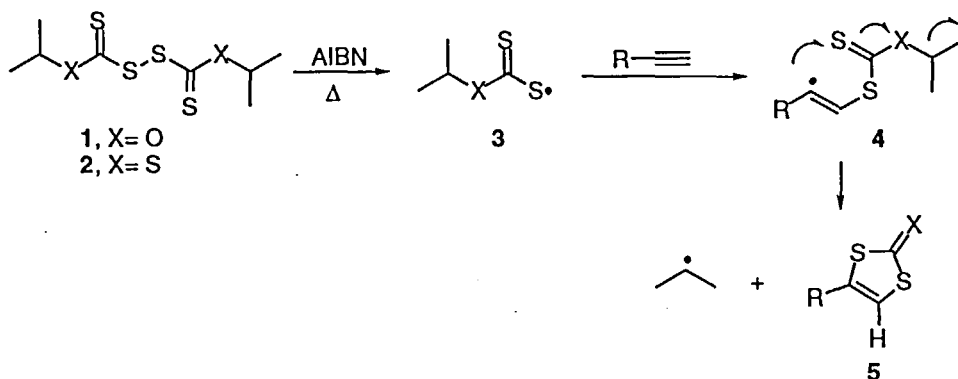
The discovery that electron rich tetrathiafulvalene (TTF) and its selenium analogue tetraselenafulvalene (TSeT) behave as molecular charge transfer agents in combination with electron poor tetracyanoquinidomethane (TCNQ), has focused much attention on those organic conductors.<sup>1,2</sup> One of the main approaches to the formation of tetrathiafulvalenes and TSeT is based on the self-condensation of 1,3-dithiol-2-one (or 1,3-dithiol-2-thione) with phosphine or phosphite.<sup>2</sup> In turn, these heterocyclic compounds may be prepared in a few steps by various methods, based on xanthate chemistry.<sup>3</sup> This communication describes a new method for the formation of 1,3-dithiol-2-one and 1,3-dithiol-2-thione in one step from alkynes and commercially available diisopropyl xanthogen 1 disulfide and thiodiisopropyl xanthogen disulfide 2. We envisioned that under radical conditions, the masked 1,3-dithiol-2-one (or 1,3-dithiol-2-thione) will give the thiyl radical 3. If generated in the presence of an alkyne, 3 will add at the less substituted position of the alkyne to form a vinyl radical 4, well positioned for a 5-*exo-trig*. cyclization on the thione. Extrusion of the isopropyl radical will sustain the radical chain process (scheme).

When a 0.2M benzene solution of the alkyne, AIBN (40% mole) and 1 was refluxed for 16-20h, compounds of type 5 could be isolated after chromatography in very good yields (Table 1). For example, 3-methoxyphenylacetylene afforded 78% yield of the desired 1,3-dithiol-2-one. When less than one equivalent of AIBN was

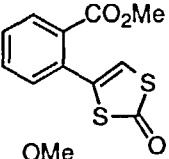
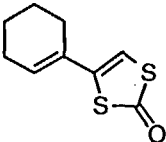
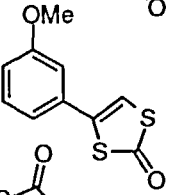
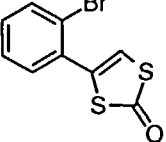
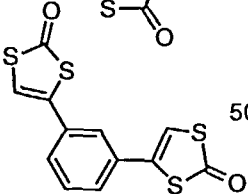
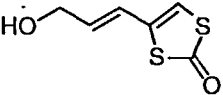
used, yield were much lower. These reaction conditions are mild and tolerated by many functional groups.

When reagent **2** was used under the same conditions with methyl-2-ethynylbenzoate, the expected 1,3-dithiol-2-thione was isolated in 54% isolated yield.

**scheme**



**Table 1: Yields of 1,3-dithiol-2-ones, from alkynes**

Product	Yield	Alkyne	Yield
	81%		76%
	78%		59%
	50%		82%

## REFERENCES

1. J. Ferrais, D.D. Cowan, V. Walalka Jr.; J.H. Perlstein; *J. Am. Chem. Soc.*, **95**, 948 (1973); R.C. Haddon, F. Wudl, M.L. Kaplan; in "Encyclopedia of Chemical Technology", 3<sup>e</sup> Ed., **20**, 674 (1982).
2. M. Narita, C.U. Pittman Jr. *Synthesis*, 489 (1976).
3. J. Boivin, E. Henriet, Z.Z. Samir; *J. Am. Chem. Soc.*, **116**, 9739 (1994); A. K. Bhattacharya, A.G. Hortmann; *J. Org. Chem.*, **39**, 95, (1974); N.F. Haley, M.W. Fichtner; *J. Org. Chem.*, **45**, 175 (1980).