Tetrahedron Letters, Vol. 34, No. 17, pp. 2763-2766, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

A Novel Synthesis of 1,3-Dithiol-2-ones from S-Propargyl Dithiocarbonates

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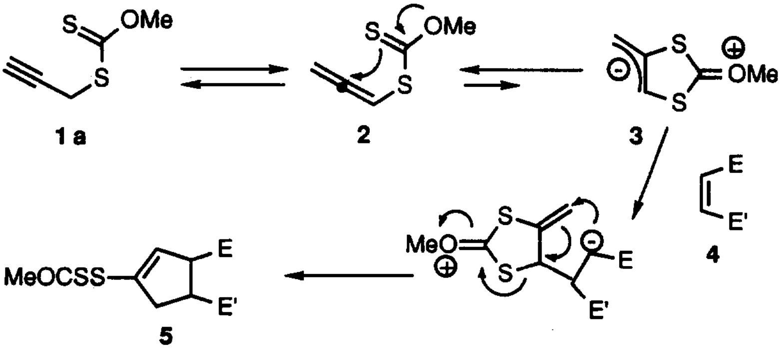
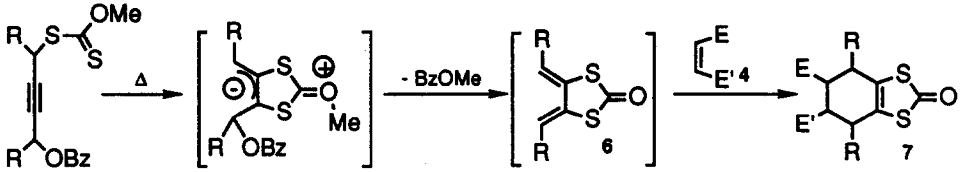
Abstract : Upon heating in chlorobenzene in the presence of a carboxylic acid, propargylic xanthates **1b-h** give the corresponding 1,3-dithiol-2-ones **10b-h** and/or **11b-h**, the former being easily isomerised to the latter with hot trifluoroacetic acid.

We recently reported[1] a new formal (3+2) annulation reaction leading to cyclopentenes of type **5** which is simply performed by heating an S-propargyl xanthate such as **1** in the presence of a highly electrophilic olefin **4**. This unusual reaction was accidentally discovered while attempting to generate and trap propargylic radicals as part of our work on the radical chemistry of xanthates[2]. Although we initially considered a radical mechanism involving a 5-endo-digonal cyclisation to explain the formation of the cyclopentene unit, subsequent experimental observations pointed rather to the intermediacy of S-allenyl xanthate **2** and possibly a betaine of novel structure **3**. Spectroscopic evidence for the former could be adduced, but the latter remained a hypothetical intermediate.



Scheme 1

We have obtained some supporting evidence for this betaine, by showing that if a suitably located potential leaving group is present in the starting xanthate, the course of the reaction is completely modified, leading instead to the hitherto unknown, highly reactive, 4,5-bis(alkylidene)-1,3-dithiolan-2-ones **6**[3], which have not been isolated but captured by an electrophilic olefin **4** to give the Diels-Alder cycloadducts **7** as shown in scheme 2 below.



Scheme 2

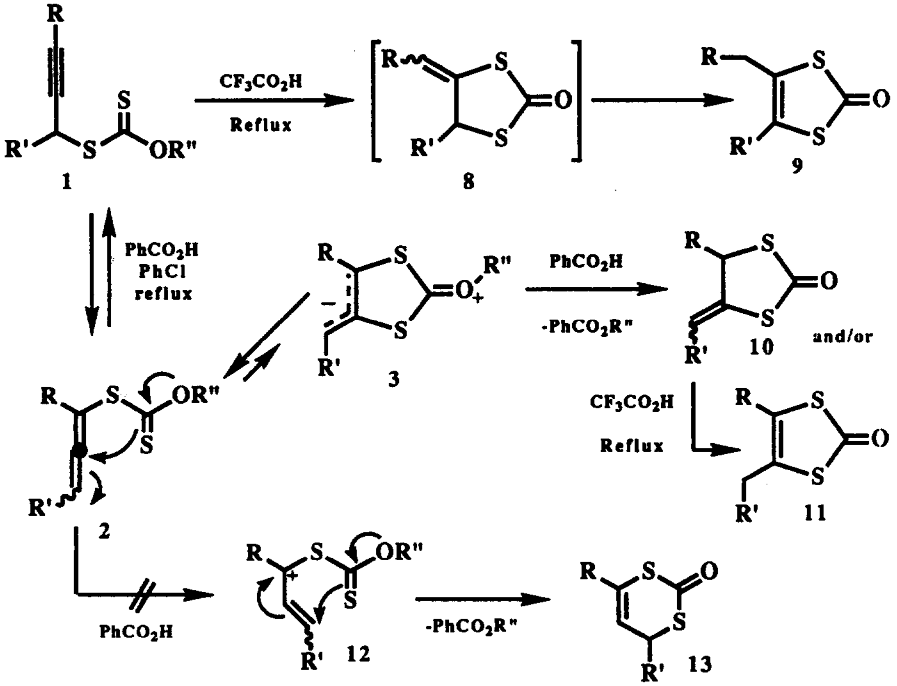
To further corroborate the intermediacy of the betaine we have carried out protonation experiments which have led to a new synthesis of 1,3-dithiol-2-ones. As outlined in scheme 3, if the propargylic xanthate is heated in the presence of a weak acid, the allylic anion subunit of betaine **3** should be protonated to give ultimately a dithiolone of structure **10** and/or **11** depending on the actual site of protonation. The acid has to be weak so as not to protonate the acetylenic group in **1** before the sigmatropic rearrangement has had a chance to occur yet strong enough to protonate the betaine. Haley and co-workers[4] had shown some years ago that in the presence of trifluoroacetic acid, S-propargyl xanthates indeed give dithiolones of type **9** arising by initial protonation of the triple bond and ring closure to give **8** followed by double bond isomerisation.

We have found that simple carboxylic acids such as benzoic or propionic acids were just right to induce the desired reaction. Thus upon heating propargylic xanthate **1b** in chlorobenzene in the presence of a slight excess of benzoic acid[5], dithiolone **11b** was obtained in good yield. In this example, protonation took place selectively since no significant amount of the corresponding isomeric dithiolone **10b** was observed. In accord with the proposed reaction scheme, methyl benzoate was also co-produced and easily identified by comparison with an authentic specimen.

Table. Reaction of xanthates **1b-f** with a carboxylic acid in refluxing chlorobenzene.

Entry	Propargylic xanthate	Carboxylic acid	Ratio of **10**:**11** (by n. m. r.)	product	yield (%)
1	**1b**	$PhCO_2H$	**11** only	**11b**	65
2	**1c**	$EtCO_2H$	1 : 1	**11c**	75
3	**1d**	$EtCO_2H$	6 : 1	**11d**	71
4	**1e**	$EtCO_2H$	6 : 1	**11e**	83
5	**1f**	$EtCO_2H$	**11** only	**11f**	68
6	**1g**	$EtCO_2H$	2 : 1	**11g**	74

This reaction was extended to a number of other propargylic xanthates as shown by the results collected in the table. Yields are generally good and, except for example **1f** which again gave only **11f**, the remaining cases resulted in mixtures of isomeric dithiolones **10** and **11**. Steric factors appear to control the site of protonation and therefore the ratio of isomers observed. In order to simplify characterisation, these were treated with hot trifluoroacetic acid so as to convert the less stable isomer into its thermodynamically more favoured companion.

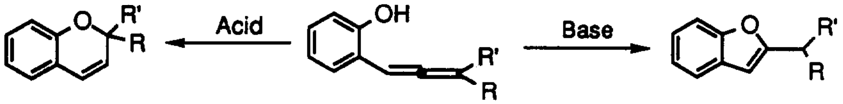


a, R = R' = H; R"= Me
b, R = Ph ; R' = H; R"= Me
c, R = Ph ; R' = Me; R"= Et
d, R = H ; R' = Me; R"= Et
e, R = H ; R' = n-C_5H_{11}; R"= Et
f, R = CH_2=CH-CH(Me) ; R' = H; R"= Et
g, R = 1-Cyclohexenyl ; R' = Me; R"= Et

Scheme 3

It is worthwhile pointing out that, in contrast to the trifluoroacetic acid mediated ring closure described by Haley et al[4] which leads to dithiolone **9**, our reaction furnishes its isomer **11** where the carbon atom originally bearing the xanthate group is now completely reduced. However, apart from its synthetic potential, this novel process provides a very strong argument in favour of the betaine intermediate. The obtention of the dithiolone structure indicates that ring closure to the betaine *precedes* the proton transfer step. If the reverse was occuring, i.e. protonation of the allene followed by ring closure, this would have led to the *six-membered dithianone* **13** *which was not observed.*

This is most striking in the case of the phenyl substituted propargylic xanthates **1b** and **1c** where protonation of the intermediate allenes **2b,c**, if it was occuring before ring closure, should lead to the highly stabilised cations **12b** and **12c** which are α- to a sulfur atom, benzylic (R= Ph), and also allylic (following rotation of the benzylic C-C bond by 90° to bring the initially orthogonal π-orbital of the double bond into overlap). Yet even in these particularly favoured instances no dithianone **13b** or **13c** are formed to any significant extent.



Scheme 4

In this context, it is interesting to compare the ring closure of o-allenyl phenols[6] (scheme 4) which under basic catalysis give benzofurans (i.e nucleophilic ring closure of the phenolate anion before eventual protonation) whereas the acid mediated reaction leads to the benzopyran derivatives (i.e. protonation to a stabilised cation precedes ring closure). It seems from our results that the thiocarbonyl sulfur is sufficiently nucleophilic to attack the central carbon of the allene to give first the betaine intermediate under essentially neutral conditions.

Acknowledgements: We wish to thank Rhône-Poulenc S.A. and the Société Nationale des Poudres et Explosifs (S.N.P.E.) for generous financial support.

References and notes

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4. Haley, N. F.; Fichtner, M. W. *J. Org. Chem.* **1980**, *45*, 2959-2962, footnote 3.
5. Typical experimental procedure: A solution of propargyl xanthate 1 (2.9 mmoles) and propionic acid (4.4 mmoles) in chlorobenzene (10 ml) was heated under reflux in an inert atmosphere for 6-10 hrs. After washing with saturated aqueous potassium carbonate, the reaction mixture was worked up in the usual way to give either the corresponding pure dithiolone **11** or the mixture of isomers **10** and **11** depending on the starting material. When a mixture was obtained, it was dissolved in trifluoroacetic acid (4 ml) and the resulting solution heated to reflux for 5 hours. After removal of the acid, the residue was dissolved in ether, and the organic layer washed with saturated aqueous potassium carbonate, dried (sodium sulfate) and evaporated to give almost pure isomer **11** in the yields shown in the table.
6. See *inter alia* : (a) Saracevic, N.; Zsindely, J.; Schmid, H. *Helv. Chim. Acta* **1973**, *56*, 1457-1476. (b) Luteijn, J. M.; Spronck, H. J. W. *J. Chem. Soc., Perkin Trans. I* **1979**, 201-203. (c) Thyagarajan, B. S.; Balasubramanian, K. K.; Rao, R. B. *Tetrahedron Lett.* **1963**, 1393-1396. (d) Grimaldi, J.; Cormons, A. *C. R. Acad. Sci., Ser. C* **1979**, *289*, 373.

(Received in France 2 February 1993; accepted 24 February 1993)