A new carbon–carbon bond forming reaction using *O*-methyl (*S*)-prop-2-ynyl dithiocarbonate

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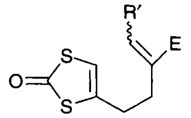
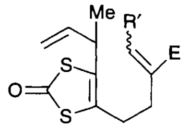
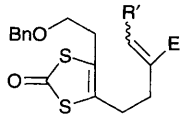
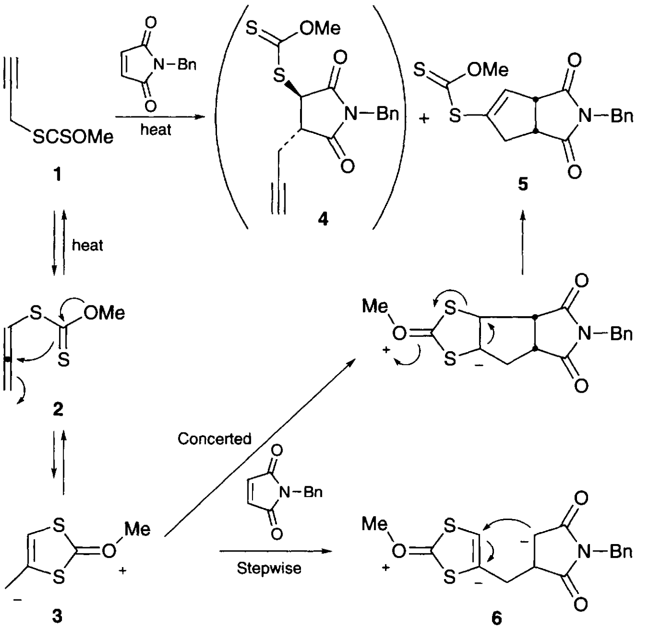
Heating *O*-methyl (*S*)-prop-2-ynyl dithiocarbonates 1a–c with electrophilic alkenes 7a–d containing nucleophilic acetoxy group gives 1,3-dithiol-2-ones 9 by a new carbon–carbon bond forming process.

O-methyl (*S*)-prop-2-ynyl dithiocarbonates **1** undergo a [3,3]-sigmatropic rearrangement upon heating to give isomeric allenes **2**. These allenes appear to be in equilibrium with cyclic betaines **3** which represent a new class of heterocycles and exhibit an interesting and useful reactivity pattern.[1] With highly electrophilic alkenes such as *N*-methyl maleimide **4**, they participate in a formal [3+2]-cycloaddition to give a cyclopentene derivative **5**,[1a] Scheme 1. This transformation may in principle proceed in a concerted or stepwise fashion and, although initial experimental observations favoured a stepwise pathway (*e.g.* maleonitrile and fumaronitrile give the same adduct but in low yield, *ca.* 20%), it seemed necessary to find more rigorous evidence for the latter route. Here we report a proof for stepwise against concertedness and, at the same time, describe a new carbon–carbon bond forming reaction. Our approach is based on the possibility of intercepting an intermediate corresponding to **6** and thus diverting the reaction from its original course.

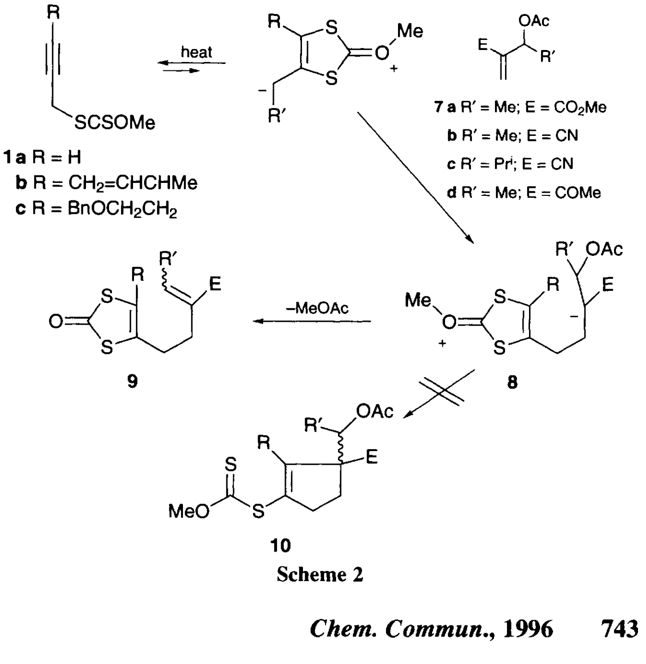
Table 1 Reaction of *O*-methyl (*S*)-prop-2-ynyl dithiocarbonates **1a–c** with alkenes **7a–d**

Dithio-carbonate **1**	Alkene **7**	Product **9**	Yield (%)
			
a	**a**	**a** R′ = Me; E = $\mathrm{CO_2Me}$	60
a	**b**	**b** R′ = Me; E = CN	90
a	**c**	**c** R′ = $\mathrm{Pr^i}$; E = CN	45
a	**d**	**d** R′ = Me; E = COMe	53
			
b	**a**	**e** R′ = Me; E = $\mathrm{CO_2Me}$	53
b	**b**	**f** R′ = Me; E = CN	65
b	**c**	**g** R′ = $\mathrm{Pr^i}$; E = CN	30
b	**d**	**h** R′ = Me; E = COMe	52
			
c	**a**	**i** R′ = Me; E = $\mathrm{CO_2Me}$	52
c	**b**	**j** R′ = Me; E = CN	65
c	**c**	**k** R′ = $\mathrm{Pr^i}$; E = CN	33
c	**d**	**l** R′ = Me; E = COMe	49

If the formal cycloaddition starts by a Michael type addition of the betaine then, in the case of an alkene such as **7**, β-elimination of the acetoxy group in intermediate **8** could take place in competition with the cyclisation step, thus leading to an open chain adduct **9** instead of the cyclopentene derivative **10**, Scheme 2. The required alkenes **7a–d** were easily prepared by the Baylis–Hillman[2] reaction using methyl acrylate, methyl



Scheme 1



Scheme 2

vinyl ketone, or acrylonitrile, and acetaldehyde or isobutyraldehyde as the aldehyde component, followed by acetylation.

Heating a neat mixture of *O*-methyl (*S*)-prop-2-ynyl dithiocarbonate **1a** with 3 equiv. of alkene **7a** at 130 °C for about 3 h furnished the 1,3-dithiol-2-one **9a** in 60% yield as a 1 : 3 mixture of geometrical isomers. These experimental conditions emerged as the most suitable from a number of preliminary trials. Comparable results were obtained using other combinations of *O*-methyl (*S*)-prop-2-ynyl dithiocarbonate and alkene. Yields varied from 33 to 90% depending on the structure of the reacting partners and, in all cases, a similar ratio (*ca.* 1 : 3) of geometrical isomers was observed.

This reaction represents a new, and somewhat unusual, carbon–carbon bond forming process. Moreover, cyclopentene derivatives of structure **10**, arising from a formal [3+2]-cyclisation, were not formed to any significant extent, indicating that β-elimination at the level of intermediate **8** is indeed faster than cyclisation. The formation of cyclopentenes such as **5** described in our first study is therefore not concerted. These results may be contrasted with the reaction of alkene **7b** with 1,3-diphenylisobenzofuran which leads by a concerted process to the normal Diels–Alder cycloadduct in 92% yield.

References

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