Diazo Transfer Reaction of 2-(Trimethylsilyl)-1,3-dithiane with Tosyl Azide. Reactivity of Transient 2-Diazo-1,3-dithiane

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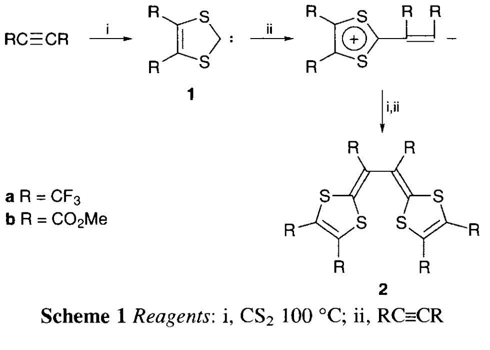
2-Lithio-2-(trimethylsilyl)-1,3-dithiane reacts with tosyl azide to give transient 2-diazo-1,3-dithiane whose reactivity towards various alkenes and alkynes is examined; an X-ray crystallographic analysis of a new bis(ketene-dithioacetal) adduct is reported.

Carbenes are reactive divalent species of great theoretical and synthetic interest.[1] In the carbene family, bis-sulfanyl substituted members have, however, received rather limited attention. A number of acyclic and cyclic dithiocarbenes have been formally generated through fragmentation of metallated orthothioformates (entailing loss of thiolate ions)[2] and/or pyrolysis (photolysis) of tosylhydrazone salts of dithiocarbonates (possibly involving intermediate diazo compounds uncapable of surviving the reaction conditions).[3] A variety of 1,3-dithiole carbenes have been instead extensively produced by deprotonation of 1,3-dithiolium salts.[4]

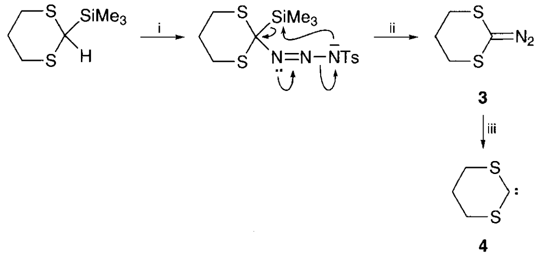
Common features of the studied dithiocarbenes were a propensity to afford tetrathioethylene products—by direct dimerisation and/or by reaction with their respective precursors—along with a reluctance to add to weakly nucleophilic alkenes. Consequently, these carbenes are normally envisaged as being relatively sluggish and poorly electrophilic intermediates as a consequence of lone pair donation by the sulfur substituents to the empty carbene orbital. Interesting results were reported for the 1,3-dithiole carbenes **1a**,**b** unusually generated by thermal reaction of carbon disulfide with perfluorobut-2-yne and dimethyl acetylenedicarboxylate.[5] The carbenes **1a**,**b** were capable of adding to their electron-poor acetylene progenitors to lead eventually to uncommon 2:1 adducts **2a**,**b** believed to occur through the path outlined in Scheme 1. This fact might suggest peculiar nucleophilic behaviour arising from especially encouraged electron donation by the sulfur atoms to form the 1,3-dithiolium aromatic structure.[5,6] However, comparative data of the chemical behaviour of differently generated dithiole carbenes **1** or other dithiocarbenes towards electrophilic substrates appear to be totally lacking.

A limiting factor for a parallel investigation of the chemical reactivity and synthetic potential of dithiocarbenes has probably been to date the lack of a straightforward entry to their 'natural' diazo precursors which indeed still represent a virtually unknown class of organic compounds. Here we report novel chemical evidence that 2-diazo-1,3-dithiane **3** can be cleanly produced upon diazo transfer reaction of 2-lithiated 2-(trimethylsilyl)-1,3-dithiane with tosyl azide under quite mild thermal conditions. Diazo group transfer of sulfonyl azides to active methylene compounds, in the presence of a base, is a well established method for the production of diazo compounds.[7] This method can also be successfully applied to poorly active methylene compounds *via* preliminary activation by formylation or benzoylation,[7] but there are no reported attempts to promote diazo transfer to unactive methylene compounds by using the silylated derivatives.

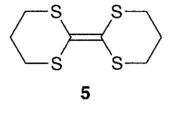


Scheme 1 *Reagents*: i, CS_2 100 °C; ii, RC≡CR

2-(Trimethylsilyl)-1,3-dithiane in a 1:20 HMPA–THF mixture was metallated with *tert*-butyllithium at −70 °C and then treated with 1 equiv. of tosyl azide (Scheme 2). The mixture was stirred at −70 °C for 2 h, then warmed to 0 °C, when evolution of nitrogen occurred. Stirring was continued for further 2 h at 0 °C and then overnight at room temp. Chromatography gave, besides tosyl amide, the bis(1,3-dithianylidene) **5** in 78% yield. The formation of the dimer **5** provides good evidence for the intermediate production of diazodithiane **3** and derived carbene **4**. The dimer **5** was previously shown to occur, but in modest yield, upon carbenoid decomposition of the sodium salt of 1,3-dithian-2-one tosylhydrazone under thermal (90–95 °C) and photochemical conditions.[3c] Analogous treatment of 2-lithio-1,3-dithiane with the tosyl azide gave none of the compound **5** and instead gave the 2-tosyl derivative in moderate amounts. This finding proves the determining role of silyl substituent in promoting a diazo transfer reaction. Attempted interception of diazo compound **3** and/or carbene **4** (over the range from −70 to 0 °C) in the presence of a slight excess of various alkenes and alkynes, including 3,4-dihydro-2*H*-pyran, 2-methylene-1,3-dithiane, diphenylacetylene, bis(trimethylsilyl)acetylene and methyl propiolate, was unsuccessful. However, in the presence of strongly electron-deficient dimethyl fumarate, the *trans*-cyclopropane **6**† was produced in 35% yield. Compound **6** was also formed, to a similar extent, when isomeric dimethyl maleate was used as a trapping agent. The non-stereospecific formation of the *trans*-adduct **6** is consistent with initial trapping of diazodithiane **3**, to give a labile pyrazoline intermediate, instead of singlet carbene **4**. Pyrazolines commonly afford cyclopropanes in a non-stereospecific fashion under thermal fragmentation.[8a] Nevertheless, this point remains unclear at this stage since some isomerization of the maleate to fumarate was found to occur under the reaction medium. More interestingly, the presumed diazodithiane **3**, in the presence of dimethyl acetylenedicarboxylate (1.5 equiv.), surprisingly led to the bisdithioacetal adduct **7a** in 66% yield (and virtually to no dimer **5**) (Scheme 3). Structural assignment of the compound **7a**



Scheme 2 *Reagents and conditions*: i, Bu^{t}Li, TsN_3, −70 °C; ii, $-TsNSiMe_3^-$; iii, $-N_2$, 0 °C



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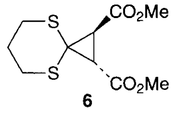

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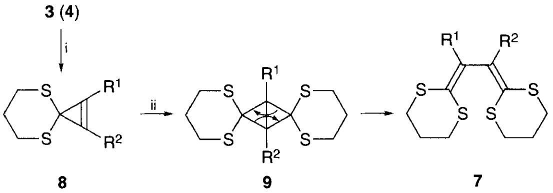
was suggested by spectral and analytical data† and confirmed by crystallographic analysis (Fig. 1).‡ The primary intervention of **3** in the formation of **7a** was substantiated by the findings that (*a*) the dimer **5** was unreactive towards the alkyne and (*b*) the lithiated silyldithiane, if not treated with tosyl azide, only exhibited nucleophilic addition to the alkyne. Similar results were also obtained with 1-tosyl-2-(trimethylsilyl)acetylene which gave the corresponding bisdithioacetal **7b**,† though in a lower yield (35%) (Scheme 3). In both cases we failed to detect any diazodithiane **3**–alkyne pyrazole adduct, which might be expected to survive our very mild reaction conditions.[8] We therefore suggest that diazodithiane **3** (or its carbene **4**) would initially add to the above electron-poor alkynes to give transient cyclopropenes **8a,b** that would be converted to strained bicyclobutanes **9a,b** by further reaction with carbene **4** and/or diazo compound **3**. The intermediates **9a,b** might in fact promptly afford the observed products **7a,b** by subsequent ring-cleavage isomerization (Scheme 3). The addition of two formal carbene units to an alkyne to give a bicyclobutane product is precedented, though to our knowledge rare.[9]

In conclusion, we have reported a new protocol for the production of 2-diazo-1,3-dithiane **3** that in principle should be of general utility for mildly forming dithio-substituted diazomethanes (and carbenes), starting from readily available silylated dithioacetals.[10]

Diazodithiane **3** seemingly was a thermolabile compound, which could undergo ready decomposition even at 0 °C presumably owing to resonance-stabilisation of derived carbene **4** by the sulfur substituents. Under our reaction conditions trapping experiments were only successful in the presence of (strongly) electron-deficient alkenes and alkynes, this fact evidently pointing to a sharp preference of the trapped species for reaction with electrophilic substrates. However, at this time, the question whether such a reactive species actually was diazodithiane **3** or ensuing carbene **4** must remain open.

Finally, the observed propensity of diazodithiane **3**/dithiocarbene **4** to transform alkynes into new bisdithioacetal adducts **7** was of special interest in view of the versatile use of the ketene dithioacetal group in organic synthesis[11] and, very recently, in the design of efficient and thermally stable NLO chromophores.[12]



8 **9** **7**

a $R^1 = R^2 = CO_2Me$ **b** $R^1 = Ts$, $R^2 = SiMe_3$

Scheme 3 *Reagents*: i, $R^1C{\equiv}CR^2$; ii, +**4** and/or **3**

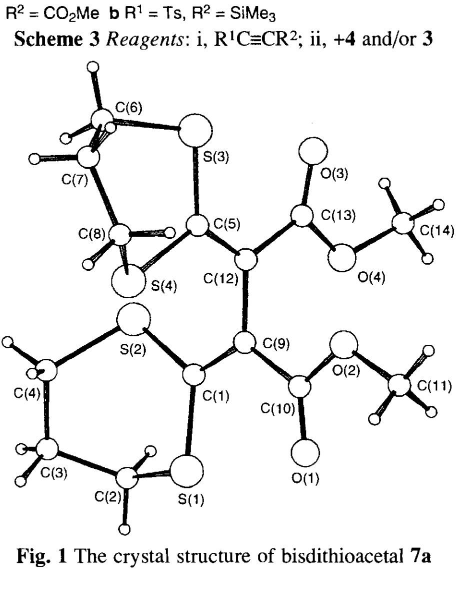


Fig. 1 The crystal structure of bisdithioacetal **7a**

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Footnotes

† The new compounds **6**, **7a** and **7b** showed correct analytical and ^1H and ^{13}C NMR and MS data.

‡ *Crystal data* for **7a**: $C_{14}H_{18}O_4S_4$, M = 378.01, monoclinic, space group $P2_1$, a = 9.064(1), b = 9.662(1), c = 10.133(1) Å, β = 100.23(5)°, U = 873.3(2) Å^3, T = 293(2) K, $F(000)$ = 396, Z = 2, D_c = 1.439 g cm^{-3}, Cu-Kα, λ = 1.54178 Å, μ(Cu-Kα) = 5.122 mm^{-1}, 1839 unique reflections used in the refinement, 2θ max = 70°. The structure was solved by direct method using SIR-92[13] and refined by fully matrix least squares on F^2 with SHELX-93.[14] The hydrogen atoms were located in a ΔF map and refined in constrained positions with isotropic thermal parameters fixed at 1.2 times the U_{iso} of the corresponding carbon atom. The final residual were R_1 = 0.0525 and wR_2 = 0.2181 for 1534 reflections having $I > 2\sigma(I)$ and R_1 = 0.0861 and wR_2 = 0.3223 for all reflections. Final goodness-of-fit was 0.983 for 1830 data and 200 parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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