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

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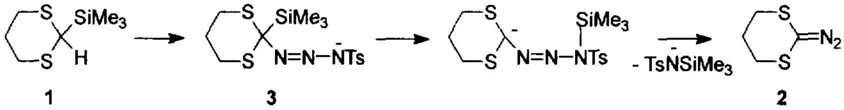
Abstract: A novel diazo transfer reaction of 2-lithiated 2-(trimethylsilyl)-1,3-dithiane with tosyl azide in a 1:20 HMPA-THF mixture furnishes 2-diazo-1,3-dithiane **2**, which decomposes at about 0 °C to give in fairly high yield bis(1,3-dithianylidene) **5** through formal dimerization of derived carbene **4**. In the presence of dimethyl fumarate, dimethyl maleate, *trans-* and *cis*-1,2-bis(benzenesulfonyl)ethylene, the diazodithiane affords only *trans*-cyclopropane adducts in a stereoselective, but non stereospecific fashion. With dimethyl acetylenedicarboxylate or 1-tosyl-2-(trimethylsilyl)acetylene, no corresponding cyclopropene adducts are observed, but instead bis(ketene-dithioacetal) products, likely arising from further reaction of cyclopropene intermediates with diazodithiane **2** and/or its carbene **4**. A related ring-opened dithioacetal product is observed upon treatment of diazodithiane with dimethyl 3,3-dimethylcyclopropene-1,2-dicarboxylate. The above reactions with electrophilic alkenes and alkynes are preferentially explained in terms of primary intervention of somewhat nucleophilic dithiocarbene **4** rather than its diazo precursor. The outcome of the usual reaction of 2-lithio-2-(trimethylsilyl)-1,3-dithiane with tosyl azide, in the presence of dimethyl acetylenedicarboxylate, is profoundly changed when performed in the absence of HMPA cosolvent. Under these circumstances the occurrence of bis(ketene-dithioacetal) product (and the dimer **5**) is essentially suppressed in favor of significant formation of the silylated maleate **12**; this is believed to arise from preferential trapping by the alkyne of the triazenyl anion **3**, the presumable progenitor of diazodithiane. An X-ray crystallographic analysis of maleate **12** is reported. © 1997 Elsevier Science Ltd.

INTRODUCTION

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.[1] With poorly active methylene compounds diazo transfer normally fails, but it can however be successfully accomplished by using an indirect deacylating strategy involving prior activation of the methylene substrate by formylation,[1] trifluoroacetylation[2] or benzoylation[3] and subsequent elimination of the activating carbonyl group in the course of the actual diazo transfer process. In recent years we have been interested in deacylating diazo transfer reactions of toluene-4-sulfonyl (tosyl) azide with various cyclic β-diones and β-keto esters.[4]

Our interest in the chemistry of diazo compounds prompted us to investigate the reaction of 2-lithiated 2-(trimethylsilyl)-1,3-dithiane **1** with tosyl azide as a potential route to 2-diazo-1,3-dithiane **2**. We reasoned that intermediate triazenyl anion **3** — which was expected should initially result from addition of dithiane anion to the terminal tosyl azide nitrogen[1a,4] — might conceivably undergo migration of the silicon moiety from carbon to tosylated nitrogen to eventually afford the diazo compound **2** (Scheme 1). Our primary aim was to uncover an unprecedented example of diazo group transfer to inactive methylene compound promoted by a silyl substituent. Our further aim was to provide the first authenticated instance of dithio-substituted diazo compound. In the family of diazo compounds, in fact, the dithio substituted members still remain practically unknown, their production having been probably achieved in a few cases upon fragmentation of tosylhydrazone salts of dithiocarbonates under thermal or photochemical conditions that avoided their possible survival.[5] The unavailability of these diazo compounds has been a limiting factor for the investigation of corresponding dithiocarbenes, whose chemical behavior and synthetic potential are to date scarcely explored. The rather few studied dithiocarbenes[5-7] are normally believed to be rather sluggish and poorly electrophilic species owing to lone pair donation by the sulfur substituents to the empty carbene orbital. However, 1,3-dithiole carbenes, unusually produced by thermal reaction of carbon disulfide with perfluorobut-2-yne and dimethyl acetylenedicarboxylate, were seemingly found to add to their strongly electron-deficient acetylene precursors to lead eventually to uncommon bis(ketene-dithioacetal) adducts.[8]

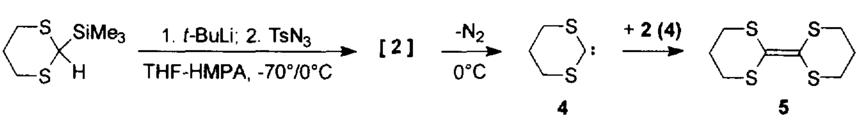


Scheme 1

Herein, we report a full account[9] of our successful diazo transfer of tosyl azide to 2-(trimethylsilyl)-1,3-dithiane **1**, including a discussion on the mechanistic and synthetic aspects of the reactivity of the ensuing diazo-compound **2** or its formally derived carbene **4**.

RESULTS AND DISCUSSION

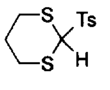
2-(Trimethylsilyl)-1,3-dithiane in a 1:20 HMPA-THF mixture was metallated with *tert*-butyllithium at -70 °C and then treated with 1 equiv. of tosyl azide at the same temperature for *ca.* 2 hr. Upon warming the reaction mixture to 0 °C, evident evolution of nitrogen occurred. Subsequent work-up and chromatography upon reaching room temperature isolated the bis(1,3-dithianylidene) **5** in 78% yield along with tosyl amide (Scheme 2).



Scheme 2

The observed occurrence of the compound **5**, the formal dimer of the dithiocarbene **4**, evidently points to the initial production of transient 2-diazo-1,3-dithiane (**2**). The same compound **5** was previously obtained, but in moderate yield, upon carbenoid decomposition of the sodium salt of 1,3-dithian-2-one tosylhydrazone under thermal (90-95 °C) and photochemical conditions.[5c] It is thus inferred that, as was anticipated, the tosyl azide can actually perform a smooth diazo transfer reaction with our silylated 1,3-dithiane **1**. The crucial role of silyl substituent in promoting a diazo transfer reaction was established by the fact that analogous treatment of 2-lithio-1,3-dithiane with the tosyl azide gave none of the dimer **5** but instead gave the 2-tosyl derivative **6** in modest yield along with major amounts of unidentified compounds.

Similar results were obtained when the above diazo transfer reaction was performed in the absence of HMPA cosolvent by using either *tert*-butyllithium or *n*-butyllithium as a metallating agent, but under both circumstances the isolated yields of the dimer **5** were significantly lower (38% and 50% respectively). Instead, replacement of the tosyl azide with 4-nitrobenzenesulfonyl azide, that in recent years has found wide use as a diazo transfer reagent,[3] proved to be quite unsatisfactory since in the presence of the latter azide the lithiodithiane **1** furnished a poor yield of the compound **5** (12%) but preferentially afforded the silylated dimer **7** presumably through an oxidative dimerization process.[10]



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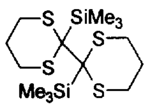

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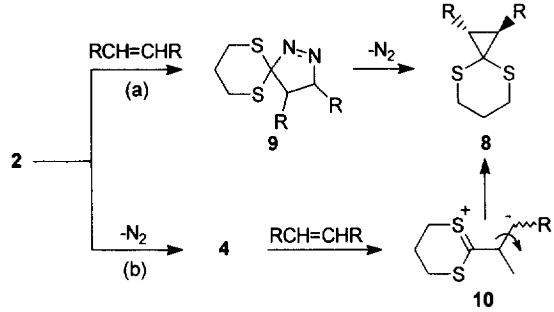
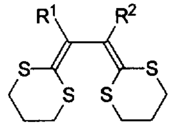
Attempted trapping of diazodithiane **2** (over the range from -70 °C to 0 °C) in the presence of a slight excess of various alkenes and alkynes, including 3,4-dihydro-2H-pyran, 2-methylene-1,3-dithiane, diphenylacetylene, bis(trimethylsilyl)acetylene and methyl propiolate, was unsuccessful, the dimer **5** being in all cases its exclusive identifiable product. However, in the presence of strongly electrophilic dimethyl fumarate and *trans*-1,2-bis(benzenesulfonyl)ethylene the respective *trans*-cyclopropanes **8a,b** could be isolated in 35 and 38% yield respectively (Scheme 3). The same compounds **8a,b** were also obtained, to a similar extent, when isomeric dimethyl maleate and *cis*-1,2-bis(benzenesulfonyl)ethylene were employed as trapping agents. The non-stereospecific formation of the *trans*-adducts **8a,b** might be ascribed to labile pyrazoline intermediates **9**, which might have been resulted from cycloaddition reactions of the diazo compound **2** with the above alkenes (Scheme 3, path a). Pyrazolines commonly afford cyclopropanes in a non-stereospecific fashion under thermal fragmentation.[11a] However, an alternate possibility consistent with the observed stereochemistry could be a two-step reaction of singlet carbene **4** with the alkenes, initially forming zwitterionic intermediates **10** (Scheme 3, path b). Zwitterionic intermediates of this type have already been invoked for reactions of (nucleophilic) singlet carbenes, including related dithiole carbenes,[8] with electrophilic alkenes and alkynes.[12] Unfortunately, our stereochemical results are further clouded by the fact that the reaction conditions caused a little isomerization of the *cis*- to the *trans*-alkenes and by the additional fact that the geometrical stability of possibly formed *cis*-cyclopropanes to the reactions conditions is presently unknown.



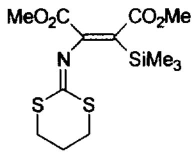
a; R = CO$_2$Me b; R = PhSO$_2$

Scheme 3

In the presence of dimethyl acetylenedicarboxylate, our usual diazo transfer reaction led to isolate the bisdithioacetal adduct **11a**[9] in high yield (80%), along with minor amounts of the dimer **5**. This reaction additionally furnished small amounts (4%) of the (previously unobserved[9]) *Z*-alkene **12**, whose structure was consistent with spectral data and fully established by an X-ray crystallographic analysis (Figure 1 and Tables 1 and 2). Besides the dimer **5**, a similar bisdithioacetal



11 (a; R = CO$_2$Me b; R = PhSO$_2$)



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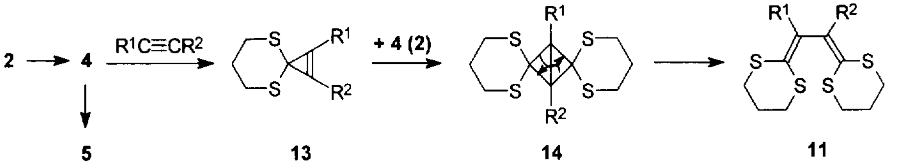
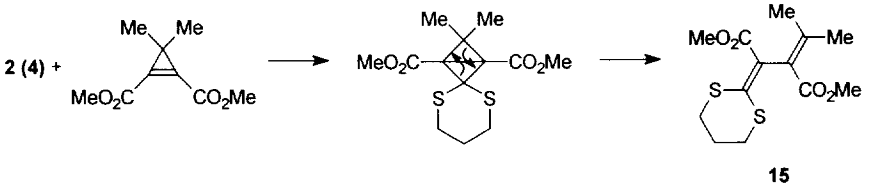
adduct **11b** was also isolated, though in a lower yield (35%), when dimethyl acetylenedicarboxylate was replaced by 1-tosyl-2-(trimethylsilyl)acetylene.

In both cases no evidence was provided for any diazodithiane **2**-alkyne pyrazole adduct, which might be expected to survive our very mild reaction conditions.[11] Moreover, control experiments established that the compound **5** was totally unreactive towards both alkynes under the reaction conditions. These findings therefore suggest that the bisdithioacetals **11a,b** were probably formed through a mechanistic route involving primary intervention of dithiane carbene **4**. Carbene **4** addition to the above electrophilic alkynes would afford transient cyclopropenes **13a,b** that could be transformed to strained bicyclobutanes **14a,b** by further reaction with **4** and/or diazodithiane **2**. The intermediates **14a,b** would eventually furnish the observed products **11a,b** by subsequent ring-opening isomerization (Scheme 4). Good support to the postulated mechanism was provided by the fact that, under the same conditions, dimethyl 3,3-dimethylcyclopropene-1,2-dicarboxylate was efficiently converted by the presumed diazo compound **2** into the ring-opened dithioacetal adduct **15** (Scheme 5).



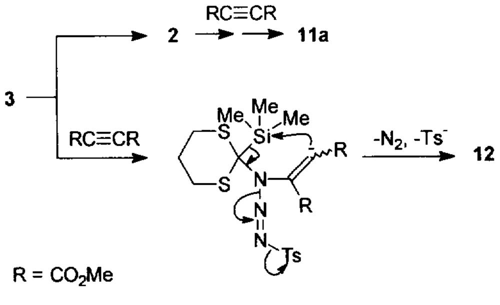
a; $R^1 = R^2 = CO_2Me$ b; $R^1 = Ts$, $R^2 = SiMe_3$

Scheme 4



Scheme 5

As for the *Z*-alkene **12**, this compound probably arose from some trapping of triazenyl anion **3** by dimethyl acetylenedicarboxylate which could occur in competition with its usual fragmentation to diazodithiane **2**. A possible mechanistic route to **12**, consistent with its *Z*-stereochemistry, might involve preliminary attack to the alkyne by the dithianyl-substituted nitrogen of the ambident anion **3** followed by migration of the silyl group to the ensuing vinylic anion (Scheme 6).



Scheme 6

The postulated route to the alkene **12** was substantiated by the finding that the absence of HMPA cosolvent significantly enhanced the formation of **12** (17%) while concomitantly causing virtual suppression of the carbenoid products **11a** and **5**. It is conceivable that, in the absence of HMPA, the unsolvatated lithium counterion[13] be essentially bound to the more electronegative tosylated nitrogen of the anion **3**. Consequently, usual migration of the silicon moiety to that nitrogen site would be greatly discouraged in favor of the postulated attack to the alkyne by the alternate dithianyl-substituted nitrogen site.

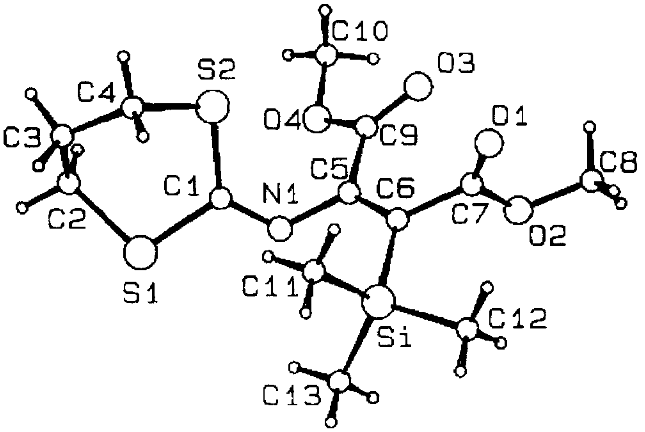


Figure 1. ORTEP plot of the maleate **12** with atom-numbering scheme.

Table 1. Atomic Coordinates (x 10^4) and Equivalent Isotropic Displacement Parameters (Å^2 x 10^3) for **12**. U(eq) is Defined as One Third of the Trace of the Orthogonalized Uij Tensor.

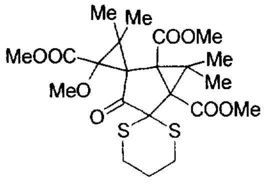
	x	y	z	U(eq)
Si(1)	9987(1)	2229(1)	7583(1)	44(1)
S(1)	6601(1)	-554(1)	3998(1)	69(1)
S(2)	4787(2)	1160(1)	5346(1)	90(1)
O(1)	8206(4)	3379(3)	9989(3)	63(1)
O(2)	9449(3)	1626(3)	11018(3)	55(1)
O(3)	6190(3)	985(3)	9697(3)	73(1)
O(4)	5660(3)	-656(3)	8157(3)	51(1)
N(1)	7478(3)	115(3)	6677(3)	41(1)
C(1)	6402(4)	239(3)	5518(3)	41(1)
C(2)	4674(6)	-640(5)	2829(4)	76(1)
C(3)	3946(7)	632(6)	2377(5)	91(2)
C(4)	4167(8)	1591(7)	3540(5)	112(2)
C(5)	7516(4)	792(3)	7952(3)	38(1)
C(6)	8566(4)	1675(3)	8504(3)	38(1)
C(7)	8653(4)	2332(4)	9889(4)	42(1)
C(8)	9616(6)	2161(6)	12418(4)	82(2)
C(9)	6395(4)	400(4)	8717(4)	42(1)
C(10)	4509(5)	-1084(5)	8765(5)	73(1)
C(11)	9019(6)	3202(6)	5993(5)	90(2)
C(12)	11413(7)	3190(7)	8922(5)	105(2)
C(13)	10921(7)	874(5)	7016(7)	101(2)

Table 2. Selected Bond Lengths [Å] and Angles [deg] for **12**.

Si(1) - C(13)	1.838(5)	O(3) - C(9)	1.199(4)
Si(1) - C(11)	1.844(5)	O(4) - C(9)	1.329(4)
Si(1) - C(12)	1.850(5)	O(4) - C(10)	1.445(4)
Si(1) - C(6)	1.903(3)	N(1) - C(1)	1.267(4)
S(1) - C(1)	1.759(3)	N(1) - C(5)	1.423(4)
S(1) - C(2)	1.808(5)	C(2) - C(3)	1.501(8)
S(2) - C(4)	1.737(5)	C(3) - C(4)	1.484(8)
S(2) - C(1)	1.752(4)	C(5) - C(6)	1.335(5)
O(1) - C(7)	1.190(4)	C(5) - C(9)	1.514(4)
O(2) - C(7)	1.346(4)	C(6) - C(7)	1.496(5)
O(2) - C(8)	1.440(4)		

C(13) - Si(1)- C(11)	109.3(3)	C(3) - C(2) - S(1)	114.3(4)
C(13) - Si(1)- C(12)	109.3(3)	C(4) - C(3) - C(2)	115.8(4)
C(11) - Si(1)- C(12)	110.6(3)	C(6) - C(5) - N(1)	121.2(3)
C(13) - Si(1)- C(6)	111.5(2)	C(6) - C(5) - C(9)	121.3(3)
C(11) - Si(1)- C(6)	109.6(2)	N(1) - C(5) - C(9)	117.3(3)
C(12) - Si(1)- C(6)	106.5(2)	C(5) - C(6) - C(7)	121.0(3)
C(1) - S(1) - C(2)	102.4(2)	C(5) - C(6) - Si(1)	123.4(2)
C(4) - S(2) - C(1)	104.4(3)	C(7) - C(6) - Si(1)	115.6(2)
C(7) - O(2) - C(8)	115.7(3)	O(1) - C(7) - O(2)	124.1(3)
C(9) - O(4) - C(10)	116.3(3)	O(1) - C(7) - C(6)	125.2(3)
C(1) - N(1) - C(5)	122.0(3)	O(2) - C(7) - C(6)	110.4(3)
N(1) - C(1) - S(2)	124.2(3)	O(3) - C(9) - O(4)	124.6(3)
N(1) - C(1) - S(1)	116.5(3)	O(3) - C(9) - C(5)	123.7(3)
S(2) - C(1) - S(1)	119.3(2)	O(4) - C(9) - C(5)	111.7(3)

Finally, we report the curious formation of the compound **16**, which was encountered when the above reaction of presumed 2-diazodithiane **2** with dimethyl 3,3-dimethylcyclopropene-1,2-dicarboxylate was repeated in neat THF. Under these circumstances the compound **16**, whose structure was fully established by X-ray crystallographic analysis, was formed to a significant extent (18%) along with major amounts of the dimer **5** (32%). There was instead almost complete suppression of the dithioacetal adduct **15** that was smoothly produced in the same reaction in the presence of HMPA. In such a case the reasons of the drastic effect of HMPA upon the reaction product outcome remain obscure.



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CONCLUSIONS

We have uncovered a novel procedure for the production of 2-diazo-1,3-dithiane **2** entailing a "desilylating" diazo transfer reaction of 2-lithio-2-(trimethylsilyl)-1,3-dithiane **1** with tosyl azide. This method should be generally applicable to the synthesis of dithio-substituted diazomethanes using readily available silylated dithioacetals.[14] Diazodithiane **2** was a labile compound undergoing ready decomposition even at 0 °C to give its carbene **4**, resonance-stabilized by the sulfur substituents. Under the employed reaction conditions, trapping experiments only succeeded with strongly electrophilic alkenes and alkynes. This fact evidently points to some nucleophilic power of the trapped species, but it remains rather unclear at this stage whether such a reactive species actually was diazodithiane **2** or derived carbene **4**. Nevertheless, despite our inconclusive stereochemical evidence, the intervention of singlet carbene **4** seems preferentially dictated by our general failure to detect any pyrazoline or pyrazole cycloadduct. Apart from mechanistic implications, the present reactions of diazodithiane **2** with alkenes and alkynes are of significant synthetic value in that they open an easy entry to otherwise (rather) inaccessible dithioacetal derivatives of functionalized cyclopropanones and, especially, α,β-unsaturated ketenes and 1,2-bisketenes. Particularly the ketene dithioacetal grouping has found versatile use in a multitude of synthetically useful transformations[15] as well as, very recently, in the design of efficient and thermally stable NLO chromofores.[16]

EXPERIMENTAL SECTION

Tosyl azide,[17] 4-nitrobenzenesulfonyl azide,[3] and dimethyl 3,3-dimethylcyclopropene-1,2-dicarboxylate[18] were prepared according to literature methods. 2-(Trimethylsilyl)-1,3-dithiane, *n*-butyllithium in hexane and *tert*-butyllithium in pentane were purchased from Aldrich. THF was distilled from sodium metal immediately prior to use. HMPA (*Caution:* it is highly toxic and suspected of being a carcinogen) was distilled from calcium hydride and stored on 13X molecular sieves activated at 200°C. All reactions involving organolithium reagents were carried out in an atmosphere of dry nitrogen. All m.p.s. (Kofler melting point apparatus) were uncorrected. Column chromatography was carried out on ICN silica gel, 63-200 60Å, by gradual elution with light petroleum (b.p. 40-70 °C) - diethyl ether mixtures (up to 100% diethyl ether) and final elution with chloroform.

Bis(1,3-dithianylidene) **5** was identified on the basis of spectral and physical data, which were consistent with those previously reported.[5c-e,6b]

^1H and ^{13}C NMR spectra were recorded on a Varian Gemini 200 or 300 instrument in $CDCl_3$ using Me_4Si as internal standard. IR spectra were recorded on a Perkin-Elmer 257 spectrophotometer. MS spectra were obtained using a VG 7070E spectrometer at an ionizing potential of 70 eV.

Reaction of 2-Lithio-2-(trimethylsilyl)-1,3-dithiane (1) with Tosyl Azide: Production and Decomposition of 2-Diazo-1,3-dithiane (2). To a solution of 2-(trimethylsilyl)-1,3-dithiane (0.5 ml, 2.66 mmol) in a mixture of dry THF (12 ml) and dry HMPA (0.6 ml) was added a solution of *tert*-butyllithium in pentane (1.55 ml, 2.66 mmol) at -70°C. After stirring for 1.5 h at -70 °C, tosyl azide (524 mg, 2.66 mmol) was added and the resulting dark-red mixture was maintained at -70 °C for 2 h (after which time it turned yellow), 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 temperature. The reaction mixture was diluted with 150 ml of *n*-hexane, washed several times with aqueous NH_3/NH_4Cl, dried (Na_2SO_4) and evaporated. Column chromatography of the residue gave 2-(1,3-dithian-2-ylidene)-1,3-dithiane **5** (78%): mp 139-141 °C (lit.[5c] mp 140-141 °C).

Acidification with hydrochloric acid of the combined aqueous washings and extraction with diethyl ether gave tosyl amide (60%).

When the same reaction was performed in neat THF the dimer **5** was isolated in 38% yield. In neat THF, but using *n*-butyllithium in hexanes (1.65 ml, 2.66 mmol), the yield of **5** was 50%.

Reaction of 2-lithio-2-(trimethylsilyl)-1,3-dithiane (1) with 4-Nitrobenzenesulfonyl Azide. Analogous treatment of **1** with 4 nitrobenzenesulfonyl azide (606 mg, 2.66 mmol) in HMPA-THF solution furnished, after usual work up and column chromatography, the compound **5** (12%), 2-(trimethylsilyl)-2-[2-(trimethylsilyl)-1,3-dithianyl]-1,3-dithiane (**7**) (42%) [mp 121-122 °C (lit.[10] mp 122 °C)] and 4-nitrobenzenesulfonyl amide (30%).

Reaction of 2-Lithio-1,3-dithiane with Tosyl Azide. 2-Lithio-1,3-dithiane [from 1,3-dithiane (330 mg, 2.66 mmol) and *tert*-butyllithium (2.66 mmol)], in 12.5 ml of a 1:20 HMPA-THF mixture was treated with

1 equiv. of tosyl azide as described above for the silylated derivative **1**. Dilution of the reaction mixture with *n*-hexane separated a pale-yellow solid. This was filtered off, washed with *n*-hexane and recrystallized from isopropyl alcohol to give 2-tosyl-1,3-dithiane (**6**) (17%), mp 150-151 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.97-2.33 (2H, m), 2.48 (3H, s), 2.50-2.63 (2H, m), 3.60-3.79 (2H, m), 4.40 (1H, s), 7.44 (2H, d, *J* = 8 Hz), 7.94 (2H, d, *J* = 8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.7, 23.7, 24.9, 60.5 and aromatic carbons; MS (m/z) 155 (0.1, M^+-119), 119 (100), 91 (8). Anal. calcd for $C_{11}H_{14}O_2S_3$: C, 48.15; H, 5.15; S, 35.05. Found: C, 48.2; H, 5.15; S, 35.0. Chromatography of the evaporated organic layer gave a mixture of unidentified products.

Production and Decomposition of 2-Diazo-1,3-dithiane (2) in the Presence of Alkenes and Alkynes. Standard Procedure. To a mixture obtained as described above by treating 2-lithio-2-(trimethylsilyl)-1,3-dithiane (**1**) with tosyl azide in HMPA-THF solution at -70 °C was added 1.5 equiv. of the appropriate alkene or alkyne. The resulting mixture was stirred at -70 °C for 1.5 h, then at 0 °C for 2 h and finally overnight at ambient temperature. Dilution with *n*-hexane, repeatedly washing with aqueous NH_3/NH_4Cl and evaporation furnished a residual material which was separated by column chromatography.

Acidification of the aqueous washings generally gave tosyl amide to a varying extent.

In the Presence of Dimethyl Fumarate. Chromatography isolated the compound **5** (10%) and dimethyl 4,8-dithiaspiro[2,5]octane-1,2-*trans*-dicarboxylate **8a** (34%), mp 143-144 °C; IR ($CHCl_3$) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.05-2.19 (2H, m), 2.87 (2H, s), 2.92-3.82 (4H, m), 3.75 (6H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 25.5, 30.6, 37.0, 37.3, 52.6, 167.2; MS (m/z) 262 (9, M^+), 203 (100), 129 (24), 85 (9); HRMS calcd for $C_{10}H_{14}O_4S_2$ 262.0334, found 262.0335. Further elution gave unidentified material.

In the Presence of Dimethyl Maleate. Chromatography gave the compound **5** (21%), the *trans*-dithiaspirooctane **8a** (38%) and a complex mixture of unidentified products.

In the Presence of trans-1,2-Bis(benzenesulfonyl)ethylene. Chromatography gave *trans*-1,2-bis(benzenesulfonyl)-4,8-dithiaspiro[2,5]octane **8b** (38%), mp 165-166 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.1-2.23 (2H, m), 2.98-3.15 (2H, m), 3.23-3.43 (2H, m), 3.83 (2H, s), 7.66-8.08 (10H, m); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 24.82, 31.6, 38.75, 55.0, 128.16, 129.7, 134.5, 139.55. Anal. calcd for $C_{18}H_{18}O_4S_4$: C, 50.7; H, 4.25; S, 30.1. Found: C, 50.6; H, 4.25; S, 30.2.

In the Presence of cis-1,2-Bis(benzenesulfonyl)ethylene. Chromatography gave the *trans*-dithiaspirooctane **8b** (29%), *trans*-1,2-bis(benzenesulfonyl)ethylene (3%) and unidentified material.

In the Presence of Dimethyl 3,3-Dimethylcyclopropene-1,2-dicarboxylate. Chromatography gave unchanged 2-(trimethylsilyl)-1,3-dithiane (15% recovery), the compound **5** (20%) and dimethyl 2-(1,3-dithian-2-ylidene)-3-isopropylidenesuccinate (**15**) (57%), as an oil; IR ($CHCl_3$) 1710, 1680 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.80 (3H, s), 2.15 (2H, m), 2.28 (3H, s), 2.94 (2H, t, *J* = 6.6 Hz), 2.98 (2H, t, *J* = 6.6 Hz), 3.66 (3H, s), 3.70 (3H, s); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 22.82, 23.66, 24.5, 29.37, 29.52, 51.92, 52.08, 122.9, 129.95, 154.32, 158.8, 165.7, 167.45; MS (m/z) 302 (100, M^+), 270 (85), 243 (40), 183 (35), 109 (31). Anal. calcd for $C_{13}H_{18}O_4S_2$: C, 51.6; H, 6.0; S, 21.2. Found: C, 51.75; H, 6.0; S, 21.1.

Further elution gave an unidentified compound (225 mg).

Using *n*-butyllithium as metallating agent, the same reaction in neat THF gave the compound **5** (32%), the succinate **15** (4%) and the dithioacetal **16** (18%), mp 162-164 °C;[19] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.27 (3H, s), 1.29 (3H, s), 1.35 (3H, s), 1.46 (3H, s), 1.83-2.15 (2H, m), 2.44 (1H, m), 2.63 (1H, m), 3.06 (1H, m), 3.31 (3H, s), 3.65 (3H, s), 3.71 (3H, s), 3.75 (3H, s), 3.85 (1H, m); MS (m/z) 486 (41, M^+), 471 (100), 454 (42), 427 (13), 119 (26), 73 (32). Anal. calcd for $C_{22}H_{30}O_8S_2$: C, 54.3 ; H, 6.2; S, 13.2. Found: C, 54.5; H, 6.2; S, 13.15.

In the Presence of Dimethyl Acetylenedicarboxylate. Chromatography gave the compound **5** (10%) and dimethyl 2-[(1,3-dithian-2-ylidene)amino]-3-(trimethylsilyl)maleate (**12**) (4%), mp 67-69 °C; IR ($CHCl_3$) 1720, 1580 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.2 (9H, s), 2.2 (2H, quintet, J = 6.6 Hz), 3.1 (4H, t, J = 6.6 Hz), 3.72 (3H, s), 3.78 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ -1.70, 22.11, 29.28, 51.77, 52.55, 132.43, 145.69, 162.49, 170.13, 170.64; MS (m/z) 347 (20, M^+), 332 (22), 288 (9), 215 (10), 184 (100), 106 (81), 73 (32). Anal. calcd for $C_{13}H_{21}NO_4S_2Si$: C, 44.9; H, 6.1; N, 4.0; S, 18.45; Si, 8.1. Found: C, 45.05; H, 6.1; N, 4.0; S, 18.4; Si, 8.1.

Further elution gave dimethyl 2,3-bis(1,3-dithian-2-ylidene)succinate (**11a**) (80%), mp 181-183 °C;[20] IR ($CHCl_3$) 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 2.15 (2H, quintet, J = 7 Hz), 2.92 (2H, t, J = 7 Hz), 2.96 (2H, t, J = 7 Hz), 3.67 (3H, s); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.4, 28.9, 29.4, 51.7, 120.9, 160.8, 162.0; MS (m/z) 378 (100, M^+); HRMS calcd for $C_{14}H_{18}O_4S_4$: 378.0088, found: 378.0085.

In neat THF the same reaction gave the maleate **12** (17%) and the succinate **11a** (4%) along with unidentified material.

In the Presence of 1-Tosyl-2-(trimethylsilyl)acetylene. Chromatography gave the compound **5** (6%) and 1,2-bis(1,3-dithian-2-ylidene)-1-tosyl-2-(trimethylsilyl)ethane (**11b**) (35%), mp 158-159 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 0.31 (9H, s), 1.88-2.02 (2H, m), 2.04-2.19 (2H, m), 2.39 (3H, s), 2.46-2.52 (2H, m), 2.73-3.13 (6H, m), 7.23 (2H, d, J = 8 Hz), 7.90 (2H, d, J = 8 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 0.4, 21.7, 23.0, 23.4, 28.7, 28.9, 29.3, 133.5, 133.8, 151.2, 151.7 and aromatic carbons; MS (m/z) 488 (5, M^+), 333 (7), 260 (9), 186 (9), 73 (100); HRMS calcd for $C_{20}H_{28}O_2S_5Si$ 488.0462, found 488.0463.

Further elution gave a complex mixture of unidentified compounds.

X-ray Crystal Structure Analysis of the Maleate 12.

Crystal data for **12**: $C_{13}H_{21}NO_4S_2Si$, M = 347.52, monoclinic, space group $P2_1$, a = 9.305(1), b = 10.497(2), c = 9.753(1) Å, β = 107.84(5)°, U = 906.8(2) $Å^3$, T = 293(2) K, $F(000)$ = 368, Z = 2, D_c = 1.273 Mg/m^3, Mo Kα, λ = 0.71689 Å, μ = 0.372 mm^{-1}. 5272 Reflections were collected, 2θ max = 60°, of which 2645 unique reflections having $I > 2\sigma(I)$ were used in the refinement. The structure was solved by direct methods using SIR-92[21] and refined by full-matrix least squares on F^2 with SHELX-93.[22] The hydrogen atoms were located in a ΔF map and refined in constrained positions with isotropic thermal parameters fixed at 1.2 times the *Uiso* of the corresponding carbon atoms. The final residual were R_1 = 0.0434, wR_2 = 0.1042. Final goodness of fit was 1.043 for 2545 reflections and 190 parameters. Atomic coordinates, thermal parameters, bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

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