COMMUNICATION

Generation and trapping of 1,3-dithian-2-ylidene-substituted ethyl carbene. On the existence of 4,8-dithiaspiro[2.5]oct-1-ene

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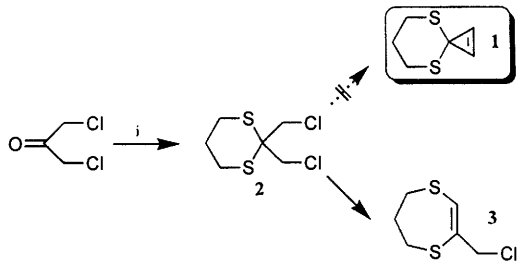
The readily available sodium salt of 2-(1,3-dithian-2-ylidene)acetaldehyde tosylhydrazone 6 could be thermolysed to transient 2-(2-diazoethylidene)-1,3-dithiane 7 and from there to 1,3-dithian-2-ylidene-substituted ethyl carbene 8. Both species gave cycloadditions with different types of alkenes. Evidence is presented for the electrocyclisation of the vinyl carbene to 4,8-dithiaspiro[2.5]oct-1-ene.

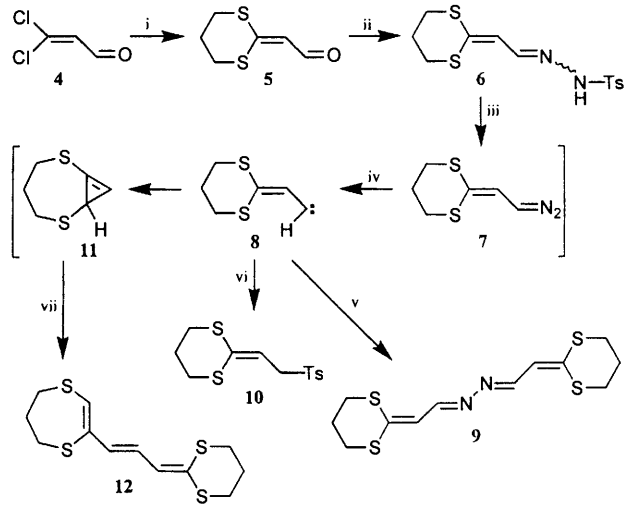
The so far unknown 4,8-dithiaspiro[2.5]oct-1-ene system **1** is of special interest as the sulfur analogue of the thoroughly investigated cyclopropene *O,O*-acetals which show an interesting cycloaddition behaviour.[1] Unfortunately, attempts to generate **1** from 1,3-dichloroacetone by analogy with the synthesis of the cyclopropenone *O,O*-acetals[1b] failed as the intermediate *S,S*-acetal **2** tends to give ring-enlargement to dithiepine **3**[2] (up to 69%) by way of an intramolecular S_N reaction (Scheme 1).[3] As vinyl carbenes can be looked upon as valence tautomers of the corresponding cyclopropenes, the chemistry of the 2,2-bis(sulfur)-functionalised vinyl carbene **8** was studied as an alternative synthesis of cyclopropene *S,S*-acetal **1**.

A promising route to the sulfur-substituted vinyl carbene **8** involves decomposition of the corresponding diazo compound **7** as formed in a Bamford–Stevens reaction under aprotic conditions (Scheme 2).[4] The required precursor **6** could be obtained conveniently from 2-(1,3-dithian-2-ylidene)acetaldehyde **5**[5] in a 4:1 ratio of *E*:*Z* isomers. Refluxing the sodium salt formed from **6** with sodium hydride or sodium methoxide in aprotic solvents, preferentially ethers like THF, 1,2-dimethoxyethane (DME) or dioxane, generated diazo compound **7** as shown by a red colour of the reaction mixture, though **7** proved to be too unstable for isolation. The tendency of **7** to eliminate nitrogen by thermolysis was demonstrated by gas evolution and the isolation of the yellow azine **9** as a combination product from **7** and carbene **8**. In the absence of a catalyst or a trapping reagent azine **9** was formed in yields up to 11%. In a competing reaction, the electrophilic carbene **8** was intercepted by the toluene-*p*-sulfinate liberated in the formation of **7** to give sulfone **10** (21%). A third decomposition product was the unstable triene **12** (7%) which is apparently formed *via* intramolecular insertion of carbene **8** into a carbon–sulfur bond giving **11**, and a subsequent reaction of **11** or a ring-enlarged carbene derived therefrom with a second molecule of **8**. However, no evidence for cyclisation of **8** to cyclopropene **1** could be obtained.

In contrast, controlled decomposition of diazo compound **7** by transition metal catalysis using dimeric rhodium(II) acetate $[Rh_2(OAc)_4]$[6,7] in THF provided the formal carbene dimerisation products *E*-**14** and *Z*-**14** (18%) (Scheme 3). Interestingly, the *E* isomer predominated by a 2:1 ratio, though the established mechanism of transition metal catalysed carbene dimerisation is known to favour the formation of *Z*-alkenes.[8] A rationale for the preferred formation of *E*-**14** would be electrocyclisation of rhodium-stabilised **8** and decomplexation to the title compound **1**, then vinylcyclopropanation of **1** by a second molecule of the rhodium carbene complex of **8** giving



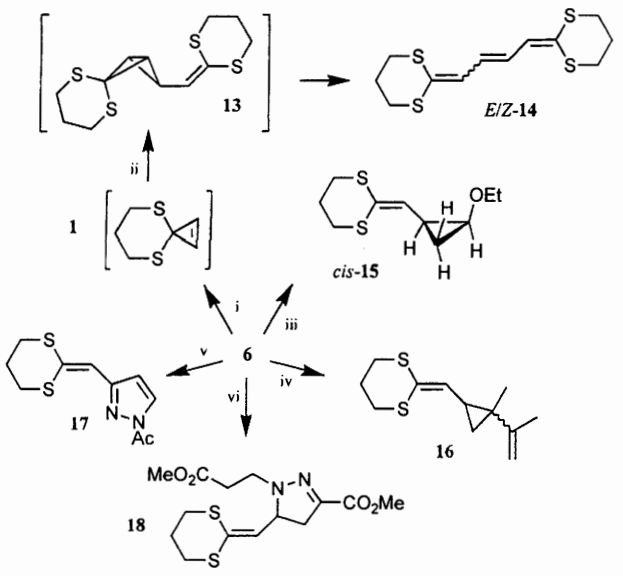
Scheme 1 *Reagents and conditions:* i, propane-1,3-dithiol, BF_3·OEt_2, CH_2Cl_2, −20 °C



Scheme 2 *Reagents and conditions:* i, 1 M NaOH, Et_2O, propane-1,3-dithiol; ii, $TsNHNH_2$, EtOH; iii, THF or DME, NaH or NaOMe, reflux, −NaTs; iv, $-N_2$; v, **7**; vi, NaTs, then H^+; vii, **8**

endo-bicyclo[1.1.0]butane **13** and from there carbon–carbon bond cleavage preferentially to *E*-**14**.[4j,9]

Irrespective of the tendency of carbene **8** to cyclise, its successful generation offered the chance to carry out trapping reactions by addition of reactive π-electron systems. As use of rhodium(II) acetate, in the decomposition of diazo compounds gives an electrophilic metal carbene species,[7] donor-substituted alkenes such as ethyl vinyl ether, vinyl acetate or 2,3-dimethylbuta-1,3-diene were employed. For optimum yields, the dry salt of **6** was suspended in an excess of the (inexpensive) trapping reagents in the presence of catalytic amounts of rhodium(II) acetate. Under these conditions, ethyl vinyl ether gave vinylcyclopropane **15** (23%) in a [2 + 1] cycloaddition with a 4:1 preference for the *cis* isomer as is to be expected for a rhodium(II) acetate-promoted cyclopropanation.[7b] An analogous [2 + 1] cyclopropanation produt **16** (15%) was obviously formed with 2,3-dimethylbuta-1,3-diene but, due to its limited stability, could only be characterised spectroscopically.



Scheme 3 *Reagents and conditions:* i, NaH, THF, then $Rh_2(OAc)_4$, reflux; ii, **8**, $Rh_2(OAc)_4$; iii, NaH, Et_2O, then excess vinyl ethyl ether, $Rh_2(OAc)_4$, reflux; iv, NaH, Et_2O, then excess 2,3-dimethylbuta-1,3-diene, $Rh_2(OAc)_4$, reflux; v, NaH, Et_2O, then excess vinyl acetate, $Rh_2(OAc)_4$, reflux; vi, NaH, Et_2O, then excess methyl acrylate, $Rh_2(OAc)_4$, reflux

Surprisingly, vinyl acetate reacted preferentially in a [3 + 2] fashion with the diazo precursor to yield 1*H*-pyrazole **17** (only 4%) after acyl migration and dehydration. Similarly, electron-deficient alkenes such as methyl acrylate gave no vinylcyclopropanation products, but two molecules of methyl acrylate reacted to yield vinyl-4,5-dihydro-1*H*-pyrazole derivative **18** (34%) by a Michael-type addition to the primary [3 + 2] cycloadduct. However, in contrast to cyclopropenone *O,O*-acetals, so far no evidence has been obtained of carbene **8** giving a cyclopentane derivative.

In conclusion, it has been demonstrated that the Bamford–Stevens reaction allows access to a novel type of bis(sulfur)-substituted propenyl carbene which may give 4π electrocylisation to the corresponding spirocyclopropene, but is also as such a versatile component in cycloaddition reactions, as is the diazo precursor.

Experimental

General procedure

To a solution of 1 equiv. of **6** in dry THF, DME or dioxane (10 ml mol^{-1}) was added under nitrogen in several portions 1.1 equiv. of NaOMe or NaH (washed with dry pentane). The mixture was stirred at room temperature for 1 h, then was refluxed overnight (in the non-catalysed process) or evaporated yielding the yellow solid sodium salt of **6** (for use in the catalysed process). This salt was refluxed in an alkene or in THF in the presence of 0.1 mol% of the rhodium catalyst for 2 h. Saturated aqueous NH_4Cl was added, the mixture extracted with dichloromethane and the combined organic layers were dried (Na_2SO_4). After removal of solvents and excess alkenes under reduced pressure the residue was chromatographed (column or flash chromatography on Machery & Nagel silica gel eluting products with light petroleum–ethyl acetate mixtures). All compounds were characterised by IR, NMR and mass spectroscopy and elemental analysis except compounds **13** and **17** (only NMR) due to their instability. *J* Values are given in Hz.

2-(1,3-Dithian-2-ylidene)acetaldehyde azine 9. δ_H(400 MHz, $CDCl_3$) 2.16–2.24 (4 H), 2.95–3.04 (8 H), 6.54 (2 H, d, *J* 9.8, 2 S_2C=CH), 8.56 (2 H, d, *J* 9.8, 2 N=CH); δ_C(100 MHz, $CDCl_3$) 23.9, 28.5, 28.8, 122.7 (2 S_2C=*C*H), 149.9 (2 S_2*C*=CH), 157.3 (2 N=CH).

2-(1,3-Dithian-2-ylidene)ethyl-*p*-tolyl sulfone 10. δ_H(400 MHz, $CDCl_3$) 2.00–207 (2 H), 2.43 (3 H, s, CH_3), 2.62 (2 H), 2.80 (2 H), 4.01 (2 H, d, *J* 8.0 CH_2Ts), 5.77 (1 H, t, *J* 8.0, S_2C=CH), 7.31 (2 H), 7.74 (2 H); δ_C(100 MHz, $CDCl_3$) 21.6 (CH_3), 24.1, 28.8, 29.2, 56.9 (*C*H_2Ts), 115.2 (S_2C=*C*H), 128.7, 129.6, 135.8, 140.1 (S_2*C*=CH), 144.6.

2-[3-(1,3-Dithian-2-ylidene)prop-1-enyl]-6,7-dihydro-5*H*-1,4-dithiepine 12. δ_H(400 MHz, $CDCl_3$) 2.10–2.23 (4 H), 2.82–2.97 (4 H), 3.33–3.50 (4 H), 6.10 (1 H, s, RSC=C*H*SR), 6.15 (1 H, d, J_{trans} 14.8, HC=CH, H-1 of the prop-1-ene chain), 6.42 (1 H, d, *J* 10.8, S_2C=CH, H-3), 6.79 (1 H, dd, J_{trans} 14.8, *J* 10.8, *H*C=CH, H-2); (100 MHz, $CDCl_3$) 24.7, 29.3, 30.0, 30.7, 30.9, 31.7, 123.1, 123.2 (both H*C*=*C*H, C-2 and C-1 of the prop-1-ene chain), 130.2 (S_2C=*C*H, C-3), 130.7 (RS*C*=CHSR), 133.0 (RSC=*C*HSR), 134.6 (S_2*C*=CH); *m/z* 288 (100%, M^+).

1,4-Bis(1,3-dithian-2-ylidene)but-2-ene *E*-14. Determination of *E*:*Z* ratio by ^{1}H NMR spectroscopy: due to its symmetry the major *E* isomer caused a typical AA'BB' spin system. δ_H(400 MHz, $CDCl_3$) 2.10–2.20 (4 H), 3.85–3.93 (8 H), 6.47 (4 H, complex multiplet, CH olefinic); δ_C(100 MHz, $CDCl_3$) 24.7, 29.2, 29.9, 127.0 (H*C*=*C*H), 130.6 (2 S_2C=*C*H), 130.7 (2 S_2*C*=CH); *m/z* 288 (100%, M^+).

1-(1,3-Dithian-2-ylidenemethyl)-2-ethoxycyclopropane *cis*-15. Determination of *cis*:*trans* ratio by ^{1}H NMR spectroscopy: the diamagnetic anisotropy effect of the vinyl group caused the downfield shift of H-1 of the major *cis* isomer. δ_H(200 MHz, $CDCl_3$) 0.70 (1 H, ddd, ^2J 6.0, J_{trans} 6.0 and 3.8 >CH*H*), 1.01 (1 H, ddd ^2J 6.0, J_{cis} 6.0 and 9.4, >C*H*H), 1.16 (3 H, t, *J* 7.0 OCH_2CH_3), 1.87 [1 H, dddd, *J* 9.6, J_{cis} 9.6 (both mixed coupling constants), J_{trans} 6.0 J_{cis} 6.0 >C*H*CH=CS_2], 2.09–2.22 (2 H), 2.80–2.93 (4 H), 3.50 (2 H, q, *J* 7.0 O*C*H_2CH$_3$ and 1 H, ddd, J_{cis} 6.0, 6.0 J_{trans} 3.8 >CHOEt, H-1), 5.75 (1 H, d, *J* 10.0, S_2C=CH); δ_C(50 MHz, $CDCl_3$) 14.5 (>CH_2), 15.0 (CH_3), 18.9 (>*C*HCH=CS_2), 25.3, 29.8, 30.6, 58.3 (>CHOEt), 66.2 (OCH_2), 123.8 (S_2*C*=CH), 133.2 (S_2C=*C*H); *m/z* 216 (73%, M^+), 187 (47, M^+ − Et), 171 (19, M^+ − OEt), 159 (45, M^+ − C_3H_5O), 119 (9, dithiane − 1), 106 (20, $C_3H_6S_2$), 85 (100).

3-(1,3-Dithian-2-ylidenemethyl)-2-methyl-2-propen-2-ylcyclopropane 16. δ_H(200 MHz, $CDCl_3$) 0.53 (1 H, dd, ^2J 4.6, J_{trans} 5.8 >CH*H*), 1.15 (3 H, s, CH_3), 1.22 (1 H, dd, ^2J 4.6, J_{cis} 9.2, >C*H*H), 1.72 (3 H, m, H_2C=CCH_3), 1.89 (1 H, ddd, *J* 9.2, J_{cis} 9.2 Hz, J_{trans} 5.8, >C*H*CH=CS_2), 2.08–2.24 (2 H), 2.80–2.90 (4 H), 4.69 (1 H, q, ^4J 1.4, =CH*H*), 4.75 (1 H, q, ^4J 0.6, =C*H*H), 5.69 (1 H, d, *J* 9.2, C*H*=CS_2); *m/z* 226 (94%, M^+), 211 (100, M^+ − Me), 119 (52, dithiane − 1).

3-(1,3-Dithian-2-ylidenemethyl)-1-acetyl-1*H*-pyrazole 17. δ_H(200 MHz, $CDCl_3$) 2.12–2.28 (2 H), 2.69 (3 H, s, $OCCH_3$), 2.97–3.08 (4 H), 6.67 (1 H, d *J* 2.8 CH, H-4 of the 1*H*-pyrazole unit), 6.72 (1 H, s, S_2C=CH), 8.17 (1 H, d, *J* 2.8, CH, H-5); δ_C(50 MHz, $CDCl_3$) 21.7 (OC*C*H_3), 23.7, 28.6, 29.1, 110.4 (CH, C-4 of the 1*H*-pyrazole unit), 116.8 (S_2C=*C*H), 128.2 (CH, C-5), 139.0 (S_2*C*=CH), 152.4 (C, C-3), 169.5 (C=O); *m/z* 240 (84%, M^+), 198 (100, M^+ − CH_2CO), 165 (45, M^+ − C_3H_7S).

5-(1,3-Dithian-2-ylidenemethyl)-3-methoxycarbonyl-1-(2-methoxycarbonylethyl)-4,5-dihydro-1*H*-pyrazole 18. δ_H(200 MHz, $CDCl_3$) 2.04–2.20 (2 H), 2.56 (1 H, dd, ^2J 17.0, *J* 12.6, C*H*H, H-4 of the 4,5-dihydro-1*H*-pyrazole unit), 2.60–2.75 (2 H, m, CH_2CO_2Me), 2.78–2.94 (4 H), 3.06 (1 H, dd, ^2J 17.0, *J* 11.0, CH*H*, H-4), 3.20–3.56 (2 H, m, NCH_2), 3.63 (3 H, s, $CH_2CO_2CH_3$), 3.75 (3 H, s, N=CCO$_2$CH_3), 4.58 (1 H, ddd, *J* 12.6, 11.0, 9.0, CHN, H-5), 5.79 (1 H, d, *J* 9.0, S_2C=CH); δ_C(50 MHz, $CDCl_3$) 24.2, 28.9, 29.3, 32.6 (*C*HH_2CO_2Me), 37.6 (*C*H_2, C-4 of the 4,5-dihydro-1*H*-pyrazole unit), 46.9 (NCH_2), 51.6 ($CH_2CO_2CH_3$), 51.9 (N=CCO$_2$CH_3), 64.6 (CHN, C-5), 127.0 (S_2C=*C*H), 134.2 (S_2*C*=CH), 139.6 (N=*C*CO$_2$Me, C-3), 162.6 (CH_2CO_2Me), 172.0 (N=C*C*O$_2$Me); *m/z* 344 (8%, M^+).

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