An Unprecedented [2+3] Cycloadditive Dimerization of a Transient Thiocarbonyl *S*-Ylide

Ibrahim El-Sayed,[a] Rita Grønbæk Hazell,[b] Jørgen Øgaard Madsen,[c] Per-Ola Norrby,[c] and Alexander Senning*[c]

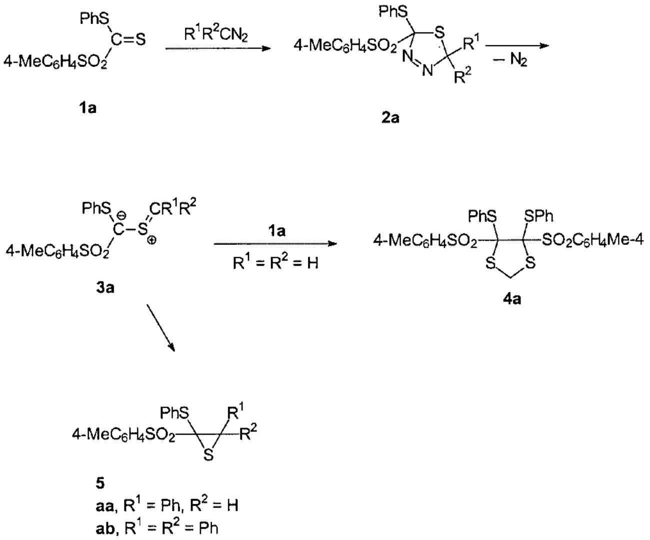
Keywords: Cycloaddition / Ab initio calculations / Sulfur / Ylides

4-Chlorophenyl *C*-(phenylsulfonyl)dithioformate reacts with diazo(trimethylsilyl)methane to form 2-(4-chlorophenylthio)-2-phenylsulfonyl-4,5-bis(trimethylsilyl)-1,3-dithiolan-1-ium (4-chlorophenylthio)(phenylsulfonyl)methylide. It is assumed that this product is formed by [2+3] cycloadditive dimerization of the transient (trimethylsilyl)methanethial *S*-[(4-chlorophenylthio)(phenylsulfonyl)methylide].

Introduction

Early in our development of the chemistry of *C*-sulfonyldithioformates **1**[1−4] we investigated the reaction between phenyl *C*-(4-methylphenylsulfonyl)dithioformate **1a** and diazomethane, diazophenylmethane, and diazodiphenylmethane.[3] The products of these reactions can be rationalized as being formed via an initial 1,3-dipolar cycloaddition of the diazoalkane to the C=S double bond, loss of nitrogen from the intermediate 2,5-dihydro-1,3,4-thiadiazole **2a** to yield the corresponding thiocarbonyl ylide **3a** which, in turn, can add to another molecule of **1a** (to yield **4a**) or, in the case of steric hindrance, cyclize (to form **5aa** and **5ab**, respectively; see Scheme 1).

These findings are in keeping with other researchers' experiences where thiocarbonyl ylides, formed from thiocarbonyl compounds and diazoalkanes, either cycloadd to extraneous 1,3-dipolarophiles or suffer a 1,3-electrocyclization to the isomeric thiirane.[5−8]



Scheme 1

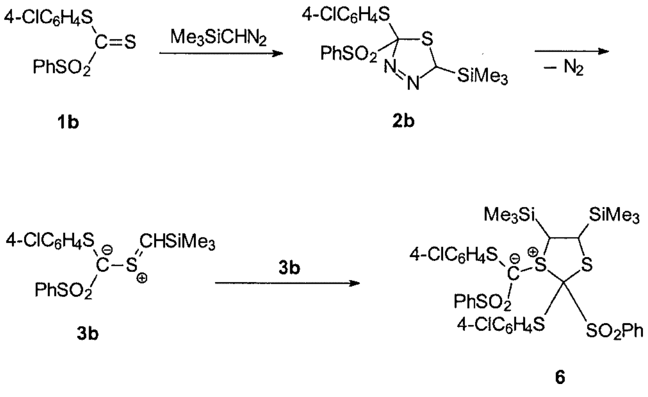
Results and Discussion

We have now found that 4-chlorophenyl *C*-(phenylsulfonyl)dithioformate (**1b**) reacts with diazo(trimethylsilyl)methane in a remarkably different fashion. In this case a thiocarbonyl ylide, i.e. (trimethylsilyl)methanethial *S*-[(4-chlorophenylthio)(phenylsulfonyl)methylide] (**3b**) is also formed in the first instance, but this then undergoes a [2+3] cyclodimerization which leads to the unsymmetrical dimer 2-(4-chlorophenylthio)-2-phenylsulfonyl-4,5-bis(trimethylsilyl)-1,3-dithiolan-1-ium (4-chlorophenylthio)(phenyl-sulfonyl)methylide (**6**; Scheme 2). A noteworthy feature of **6** is its quasi-head-to-head structure with the onus of vicinal bulky

---

[a] Chemistry Department, Faculty of Science, Menoufia University,
Shebin El-Kom, Egypt
Fax: (internat.) + 20-2/3904250
E-mail: eltantawy_2000@yahoo.com
[b] Department of Chemistry, Aarhus University,
8000 Århus C, Denmark
Fax: (internat.) + 45/86196199
E-mail: haz@chem.au.dk
[c] Department of Chemistry, Technical University of Denmark, DTU 207,
2800 Kgs. Lyngby, Denmark
Fax: (internat.) + 45/45933968
E-mail: aes@kemi.dtu.dk
jom@kemi.dtu.dk
pon@kemi.dtu.dk

trimethylsilyl groups. The structure of **6** was elucidated by elemental analysis, spectroscopy, and single-crystal X-ray crystallography (Figure 1).[9]



1b **2b** **3b** **6**

Scheme 2

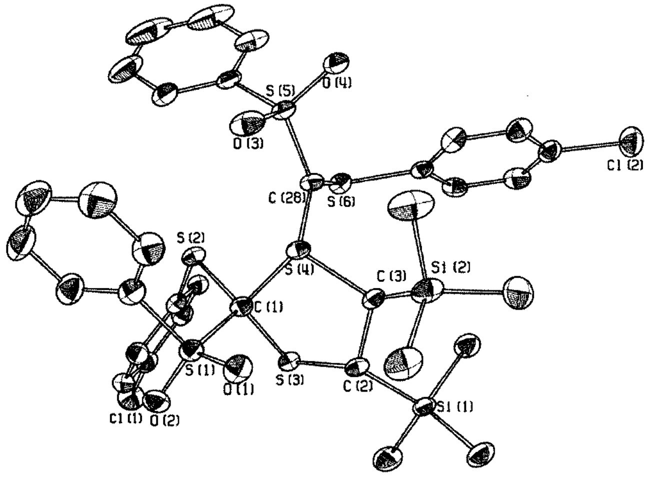
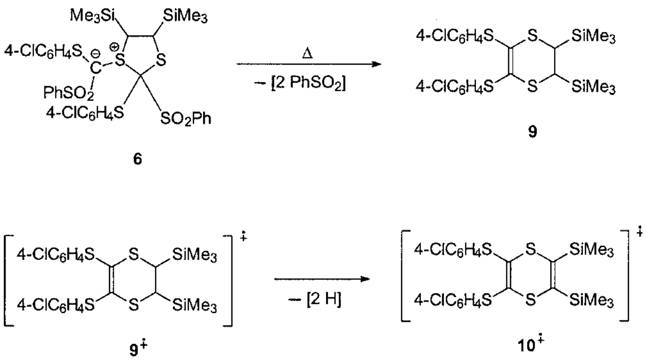


Figure 1. The molecular structure of **6** (50% probability ellipsoids; H atoms omitted); selected distances (Å): C(1)−S(1) 1.856(2), C(1)−S(2) 1.808(2), C(1)−S(3) 1.791(2), C(1)−S(4) 1.916(2), S(4)−C(3) 1.847(2), C(2)−C(3) 1.527(4)

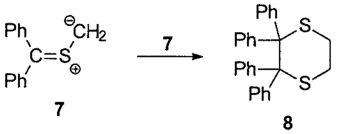
An attempt to record the direct-inlet EI mass spectrum of **6** revealed an interesting pyrolysis in the inlet system. Thermal loss of two phenylsulfonyl groups and subsequent rearrangement leads to the formation of dihydro-1,4-dithiin **9** whose molecular ion, $\mathbf{9}^{+\cdot}$, can be observed at $m/z = 546$, together with a peak at $m/z = 544$, corresponding to the loss of two hydrogen atoms to form $\mathbf{10}^{+\cdot}$ (Scheme 3). The CI, MALDI, and FAB$^+$ mass spectra also failed to produce a molecular ion signal for **6**.



6 **9** $\mathbf{9}^{+\cdot}$ $\mathbf{10}^{+\cdot}$

Scheme 3

Fluorinated thioketones have been found to react with diazobis(trimethylstannyl)methane to form unsymmetrical azines[11] in a manner unrelated to our present observations. Huisgen et al.[12] have reported the two-step, head-to-head symmetrical dimerization of diphenylmethanethione *S*-methylide **7** → **8** (Scheme 4), but this still means that our unsymmetrical dimerization of **5**, with one molecule acting as a 1,3-dipole and the other as a 1,3-dipolarophile (Scheme 2), is unprecedented.



7 **8**

Scheme 4

In order to rationalize the observed selectivities we performed B3LYP/6−31+G* calculations with the Jaguar program[13] on a model system, **11**, where the aryl groups of **3b** have been replaced by methyl groups. We also calculated **11** and the corresponding dimer **12** by MNDO(d) with Spartan (cf. Scheme 5).[14] The computational model was first validated by a comparison of the MNDO(d) dimer **12** with the X-ray structure of **6**. The results show fair agreement, with bond lengths generally being reproduced to within a few hundredths of an ångström. The structures of **11** from the two computational models also agreed well, a good indication that the computational level is well converged. The computed structure is most closely related to the resonance structure shown, with the negative charge of the ylide in the position where it is best stabilized by the adjacent sulfonyl moiety, and the double bond therefore between the central sulfur and the silyl-substituted carbon atom. The frontier orbitals are closely reminiscent of those of the allyl anion, the orbital energies being lowered by the presence of the cationic sulfur atom, and the LUMO therefore capable of acting as an electrophile. As can be seen the LUMO is skewed towards the $C=S^+$ double bond, and antibonding, a rationale for the fact that this bond, and not the C-S$^+$ single bond, acts as the electrophile. The HOMO, acting as the nucleophile, has a node plane in analogy to the HOMO of the allyl anion, and overlaps well with the LUMO of another monomer molecule, leading to the observed [2+3] reactivity. What remains to be explained is the head-to-head regioselectivity. The relative sizes of the FMOs lead to no preference for one attack over the other. Thus we conclude that the regioselectivity must be charge controlled with the most negative carbon atom attacking the positive sulfur atom.

Scheme 5

Experimental Section

6: Diazo(trimethylsilyl)methane[15] (2 M hexane solution, 0.50 mL, 1.01 mmol) was added dropwise to a stirred solution of 4-chlorophenyl *C*-(phenylsulfonyl)dithioformate (**1b**)[3] (300 mg, 0.91 mmol) in 15 mL of dry diethyl ether under argon at −78 °C,. The reaction mixture was allowed to warm to room temperature over 3 h, after which time the red color of **1b** had disappeared. Evaporation of the solvents under reduced pressure left a colorless solid residue which was recrystallized from diethyl ether/hexane (3:1) to afford **6** (347 mg, 92% yield) as colorless crystals, m.p. 161−162 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = -0.01$ (s, 9 H), 0.38 (s, 9 H), 3.32 (d, $^{3}J = 13.2$ Hz, 1 H); 3.50 (d, $^{3}J = 13.6$ Hz, 1 H), 7.16−7.35 (m, 11 H), 7.50 (d, $^{3}J = 8.4$ Hz, 2 H), 7.60−7.80 (m, 2 H), 7.86−7.90 (m, 1 H), 8.19 (d, $^{3}J = 7.6$ Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = -1.22$ (q), 0.04 (q), 41.45 (d), 58.23 (d), 61.20 (s), 107.77 (s), 127.01 (d), 127.54 (d), 127.57 (d), 128.04 (d), 128.72 (d), 128.98 (d), 129.03 (d), 131.29 (s), 131.67 (s), 132.76 (d), 134.82 (d), 134.96 (s), 137.20 (s), 137.37 (d), 139.57 (s), 144.76 (s) ppm. IR (KBr): $\tilde{\nu} = 3040$, 2973, 2825, 1475, 1303, 1142, 1086, 851, 687 cm^{-1}. MS: no molecular ion observable by EI, CI, MALDI, or FAB^{+} techniques. $C_{34}H_{38}Cl_2O_4S_6Si_2$ (830.1): calcd. C, 49.19, H 4.61, Cl 8.54, S 23.18; found C 49.17, H 4.58, Cl 8.58, S 23.32.

---

[1] S. Holm, A. Senning, *Tetrahedron Lett.* **1973**, 2389−2392.

[2] A. Senning, *Sulfur Lett.* **1991**, *12*, 235−246.

[3] I. El-Sayed, M. F. Abdel-Megeed, S. M. Yassin, A. Senning, *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *86*, 239−257.

[4] S. M. Yassin, *Sulfur Rep.* **1995**, *16*, 343−360.

[5] P. K. Claus, *Houben-Weyl* **1985**, *E11*, 1344−1359.

[6] W. G. Whittingham, in *Comprehensive Organic Group Transformations* (Eds.: A. R. Katritzky, O. Meth-Cohn, C. W. Rees), Pergamon, Oxford, **1995**, Vol. 3, pp. 367−368.

[7] [7a] G. Mloston, H. Heimgartner, *Polish J. Chem.* **2000**, *74*, 1503−1532. [7b] G. Mloston, H. Heimgartner, in *The Chemistry of Heterocyclic Compounds, Vol. 59: Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocyclic and Natural Products* (Eds.: A. Padwa, W. Pearson), John Wiley & Sons, New York, 2002, pp. 315−360.

[8] [8a] M. Böhshar, J. Fink, H. Heydt, O. Wagner, M. Regitz, *Houben-Weyl* **1990**, *E14b*, 1369. [8b] M. Mikolajczyk, J. Drabowicz, P. Kielbasinski, *Houben-Weyl* **1996**, *E21*, 5046−5048.

[9] X-ray structure analysis: Crystals of **6** are monoclinic, space group $P2_1/n$ at 120 K: $a = 11.671(1)$ Å, $b = 17.392(2)$ Å, $c = 19.267(2)$ Å, $\beta = 91.125(2)°$, $V = 3942(1)$ Å^3, $Z = 4$, $\rho_{calcd.} = 1.398$, $\mu = 0.58$ mm^{-1} (Mo-K_α radiation, $\lambda = 0.71073$ Å), $F(000) = 1728$. Of 37359 reflections collected on a SMART diffractometer, 11831 were independent, 7517 significant [$I > 3\sigma(I)$]. The structure was solved by means of the SIR97 program system.[10] Least-squares refinement of 433 parameters, final $R = 0.041$, $R_w = 0.049$. CCDC-186837 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[10] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, M. C. Burla, G. Polidori, M. Camalli, R. Spagna (1997), SIR97, University of Bari, Italy; cf. A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Molterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115−119.

[11] J. Hasserodt, H. Pritzkow, W. Sundermeyer, *Liebigs Ann.* **1995**, 95−104.

[12] I. Kalwinsch, X. Li, J. Gottstein, R. Huisgen, *J. Am. Chem. Soc.* **1981**, *103*, 7032−7033.

[13] http://www.schrodinger.com.

[14] http://www.wavefun.com.

[15] T. Shioiri, T. Aoyama, in *Encyclopedia of Reagents for Organic Synthesis* (Ed.: L. A. Paquette), John Wiley & Sons, Chichester, **1995**, pp. 5248−5251.

Received October 10, 2002
[O02558]