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Generation and Trapping of Dichlorothioketene

Gunadi Adiwidjaja[a], **Carola Kirsch**[b], **Flemming Pedersen**[c], **Ernst Schaumann**[+)*b], **Gerd C. Schmerse**[b], **and Alexander Senning**[c]

Mineralogisch-Petrographisches Institut der Universität Hamburg[a],
Grindelallee 48, W-2000 Hamburg 13, F.R.G.

Institut für Organische Chemie der Universität Hamburg[b],
Martin-Luther-King-Platz 6, W-2000 Hamburg 13, F.R.G.

Kemisk Institut, Aarhus Universitet[c],
Langelandsgade 140, DK-8000 Århus C, Denmark

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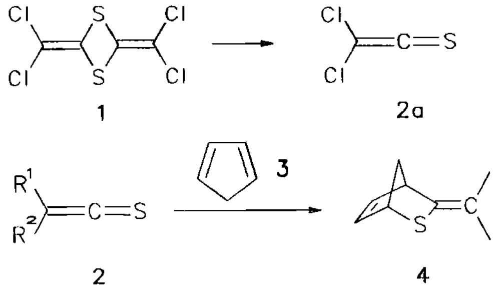
Flash-vacuum pyrolysis of 2,4-bis(dichloromethylene)-1,3-dithietane (**1**) at 820°C furnishes dichlorothioketene (**2a**) which may be trapped with cyclopentadiene (**3**) in a [4+2] cycloaddition. The constitution **4a** of the product is confirmed by an X-ray structural analysis of the related cycloadduct **4b**.

Because of its ready accessibility and high reactivity, dichloroketene is one of the most important ketenes[1)]. Therefore, the corresponding sulfur compound is of particular interest. In fact, dichlorothioketene (**2a**) has been generated by base-induced [3+2] cycloreversion of a 1,3-dithiolane derivative. However, on attempted trapping with electrophiles, oligomerization prevails[2)]. Obvious alternatives providing **2a** involve flash-vacuum pyrolyses (FVP) of the appropriate 1,2,3-thiadiazole or 2,4-dialkylidene-1,3-dithietane. The latter route has become potentially feasible after a synthesis of the dichlorothioketene dimer **1** from non-thioketene precursors has been developed[3)].



2, 4 a : $R^1 = R^2 = Cl$
b : $R^1 = Ph, R^2 = iPr$

Thioketene generation by [2+2] cycloreversion in FVP experiments is usually hampered by the low volatility of the dimers involved[4)]. This is not true in the cleavage of **1**, but relatively high temperatures are required. Thus, **1** is recovered unaltered from the cold finger of the FVP apparatus on attempted pyrolysis at 720°C, while, on the other hand, considerable uncontrolled decomposition occurs at 880°C. Optimal conditions are found at 820°C, but at the expense of only partial conversion of **1** into **2a** since the typical thioketene color[5)] cannot be observed.

In previous experiments, 1,3-cyclopentadiene (**3**) has proven to be an efficient scavenger of thioketenes[5)]. However, attempts to trap **2a** by inclusion in a trichlorofluoromethane matrix at −196°C and subsequent condensation of **3** have failed to give an adduct. This indicates that **2a** is extremely unstable, even at very low temperatures.

Trapping of **2a** has first been achieved by collection of the pyrolysis products of **1** on a matrix of solid neat **3**. Upon melting of the matrix, a 1:1 adduct can be isolated, albeit in moderate yield. The spectroscopic evidence suggests constitution **4a** for this adduct, corresponding to a [4+2] cycloaddition reaction between the C=S part of the heterocumulene **2a** and the 1,3-diene system of **3**. Alternative structures involving the heterocumulene C=C bond in the cycloaddition are clearly ruled out by the absence of a visible color (as expected for a thioketone) and of a C=S signal in the ^{13}C-NMR spectrum of the adduct.

Constitution **4a** has finally been confirmed by an X-ray structural investigation of the related cycloadduct **4b** which is obtained from thioketene **2b** and **3** and gives very similar NMR data. The X-ray analysis reveals the product to be a thianorbornene derivative (Figure 1, Tables 1, 2). The single diastereomer which has been isolated has the *E* configuration. The phenyl substituent adopts an almost orthogonal orientation with respect to the fairly planar alkenyl sulfide moiety S2(C4)−C3=C8(C81)−C9 (interplanar angle 86.6°).

Parallel experiments with **2a** and 5-isopropylidene-1,3-cyclopentadiene and 2,3-dimethyl-1,3-butadiene, respectively, have failed to furnish well-defined adducts.

Thus, dichlorothioketene (**2a**) has been generated by flash-vacuum pyrolysis of **1** and can, in spite of its low stability, be unequivocally characterized by its [4+2] cycloaddition behavior. Since previous attempts to trap **2a**, generated at −50°C, have failed[2)] it

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[+)] Present address: Institut für Organische Chemie, Techn. Univ. Clausthal, Leibnizstraße 6, W-3392 Clausthal-Zellerfeld, F.R.G.

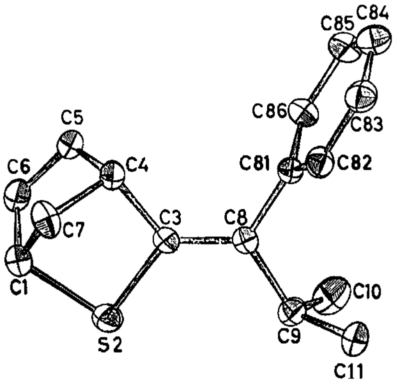

Figure 1.
Molecular structure of **4b** (ORTEP, 50% probability level)

appears that **2a** can only be utilized at substantially lower temperatures (≥ −196°C).

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Experimental

3-(Dichloromethylene)-2-thiabicyclo[2.2.1]hept-5-ene (**4a**): By analogy with our reported procedure[6], compound **1**[3] was sublimed at 50−80°C into the pyrolysis tube of a flash-vacuum pyrolysis apparatus and pyrolyzed at 820°C/10^{-4} to 10^{-3} Torr. The pyrolysis products were allowed to condense on a matrix of solid 1,3-cyclopentadiene (**3**) kept at −196°C. After thawing at −78°C, the reaction products were collected and subjected to chromatography with a Chromatotron apparatus (Model 7924 T, Harrison Research) on silica gel (Merck 60, eluent pentane). A light yellow oil was isolated, yield 4% (31%, based on consumed **1**). − ^{1}H NMR ($CDCl_3$): δ = 1.88, 1.97 (m; 1 H, each, CH_2), 4.16 (m; 1 H, bridgehead CH), 4.45 (m; 1 H, bridgehead SCH), 6.29, 6.55 (dd, *J* = 3/6 Hz; 2 H, olefinic CH=CH). − ^{13}C NMR ($CDCl_3$): δ = 52.84, 56.48 (C-1, -4), 54.86 (C-7), 104.50 (CCl_2), 132.73, 138.56 (C-5, C-6), 144.6 (C-3).

$C_7H_6Cl_2S$ (193.1)	Calcd.	Cl 36.72 S 16.61
	Found	Cl 37.05 S 16.53

Molecular mass Calcd. 191.9567 Found 191.9570 (MS)

(E)-3-(2-Methyl-1-phenylpropylidene)-2-thiabicyclo[2.2.1]hept-5-ene (**4b**): As described previously[6], 5-isopropyl-4-phenyl-1,2,3-thiadiazole was pyrolyzed at 530°C and at least 10^{-3} Torr. Thioketene **2b** was collected on the cold finger of the flash-vacuum pyrolysis apparatus together with dichloromethane. The solid was allowed to melt by addition of ethanol into the cold finger, and the resulting solution was dropped into a flask with a twofold excess of freshly distilled 1,3-cyclopentadiene (**3**), kept at −78°C. After warming to room temp., evaporation provided an almost quantitative yield of pure **4b**, m.p. 75°C. − ^{1}H NMR ($CDCl_3$): δ = 0.85 and 1.07 (d, *J* = 7 Hz; 6 H, CH_3), 1.60, 1.74 (m; 1 H each, CH_2), 2.60 (sept, *J* = 7 Hz; 1 H, *i*Pr-CH), 3.38 (m; 1 H, bridgehead CH), 4.30 (m; 1 H, bridgehead SCH), 5.90, 6.34 (dd, *J* ≈ 3/6 Hz; 2 H, olefinic CH=CH), 7.0−7.4 (m; 5 H, Ph). − ^{13}C NMR ($CDCl_3$): δ = 20.8, 21.2 (CH_3), 37.5 (*i*Pr-CH), 50.5, 53.4 (C-1, -4), 53.8 (C-7), 126.4−129.8 and 140.7 (Ar-C), 132.9, 135.7 (C-5, -6), 137.3, 139.0 (*C*Ph, C-3).

$C_{16}H_{18}S$ (242.4)	Calcd.	C 79.29 H 7.48 S 13.23
	Found	C 79.10 H 7.47 S 13.10

Crystal Structure Determination of **4b**[7]: Rotating-crystal, Weissenberg, and precession photographs of a crystal with dimensions 0.35 × 0.42 × 0.55 mm gave approximate lattice constants and the preliminary space group. Refinement of the lattice constants led to the following cell dimensions:

a = 734.9(1), *b* = 1226.2(2), *c* = 1565.9(3) pm, α = 76.97(2)°, β = 88.89(2)°, γ = 88.83(2)°, *V* = 1.374 · 10^9 pm^3, space group $P\bar{1}$, *Z* = 4 with two independent molecules, $d_{\text{calcd.}}$ = 1.18 g · cm^{-3}.

Intensity measurements were carried out on a Syntex $P2_1$ single-crystal diffractometer by using Mo-K_α radiation monochromated with graphite in the θ-2θ scan technique with variable scan speed (1−29°/min; scan width Δϑ = 0.5 + 0.34 · tanθ). The intensity data were not corrected for absorption. The measured intensities were reduced to 3395 symmetry-independent reflexions. The structure was solved by the direct-methods program MULTAN[7]. The *E* maps revealed the positions of all the heavy atoms. After the refinement of these positions the H atoms were found from a Fourier synthesis[8]. In the final refinement, convergence was achieved at

Table 1. Selected interatomic distances between non-hydrogen atoms [pm] and angles [°] with standard deviations in units of the last significant figure in parentheses for **4b**

C1 - S2	186.8 (3)	C1 - C6	150.0 (4)
C1 - C7	153.1 (4)	C3 - S2	178.6 (2)
C3 - C4	153.6 (3)	C3 - C8	133.2 (3)
C4 - C5	151.6 (3)	C4 - C7	155.2 (3)
C5 - C6	132.5 (4)		
C8 - C9	152.3 (3)		
C6 - C1 - C7	101.8 (2)	S2 - C1 - C7	100.9 (2)
S2 - C3 - C4	107.4 (2)	C1 - S2 - C3	89.8 (1)
C4 - C3 - C8	128.3 (2)	S2 - C3 - C8	124.4 (2)
C3 - C4 - C7	103.3 (2)	C5 - C4 - C7	100.1 (2)
C4 - C5 - C6	108.2 (2)	C5 - C6 - C1	108.4 (2)
C1 - C7 - C4	95.0 (2)	C3 - C8 - C9	121.9 (2)
C3 - C8 - C81	120.0 (2)	C9 - C8 - C81	118.1 (2)

Table 2. Atomic fractional coordinates and equivalent isotropic parameters [$Å^2$] with standard deviations in parentheses for the two independent molecules of **4b** (atom/atom + 50) $U_{eq} = 1/3 \sum_i \sum_j (U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j)$

Atom	x	y	z	U_{eq}
S2	0.0271 (1)	0.3323 (1)	0.9594 (1)	0.056 (1)
C1	-0.1902 (5)	0.3820 (3)	0.9024 (2)	0.056 (2)
C3	-0.0909 (4)	0.2193 (2)	1.0289 (2)	0.042 (2)
C4	-0.2906 (4)	0.2283 (3)	1.0005 (2)	0.047 (2)
C5	-0.3707 (4)	0.3319 (3)	1.0256 (2)	0.055 (2)
C6	-0.3082 (5)	0.4210 (3)	0.9692 (2)	0.062 (2)
C7	-0.2768 (5)	0.2705 (3)	0.8996 (2)	0.060 (2)
C8	-0.0137 (4)	0.1435 (2)	1.0930 (2)	0.042 (2)
C9	0.1888 (4)	0.1444 (3)	1.1115 (2)	0.051 (2)
C10	0.2850 (5)	0.0332 (3)	1.1107 (3)	0.070 (3)
C11	0.2233 (5)	0.1783 (4)	1.1969 (3)	0.102 (4)
C81	-0.1275 (4)	0.0556 (2)	1.1510 (2)	0.040 (2)
C82	-0.1456 (4)	-0.0500 (2)	1.1331 (2)	0.049 (2)
C83	-0.2527 (5)	-0.1307 (3)	1.1865 (3)	0.060 (2)
C84	-0.3404 (5)	-0.1071 (3)	1.2593 (3)	0.065 (3)
C85	-0.3238 (5)	-0.0036 (4)	1.2782 (2)	0.069 (3)
C86	-0.2180 (4)	0.0783 (3)	1.2240 (2)	0.057 (2)
S52	-0.4882 (1)	0.5675 (1)	0.7438 (1)	0.053 (1)
C51	-0.7002 (4)	0.4939 (3)	0.7901 (2)	0.055 (2)
C53	-0.5980 (4)	0.6146 (2)	0.6408 (2)	0.043 (2)
C54	-0.7886 (4)	0.5638 (3)	0.6497 (2)	0.048 (2)
C55	-0.8954 (4)	0.6237 (3)	0.7095 (2)	0.058 (2)
C56	-0.8416 (5)	0.5836 (3)	0.7913 (2)	0.061 (2)
C57	-0.7605 (5)	0.4475 (3)	0.7123 (2)	0.058 (2)
C58	-0.5245 (4)	0.6824 (3)	0.5706 (2)	0.045 (2)
C59	-0.3282 (4)	0.7213 (3)	0.5690 (2)	0.055 (2)
C60	-0.2112 (5)	0.6716 (3)	0.5051 (3)	0.079 (3)
C61	-0.3123 (6)	0.8487 (3)	0.5478 (3)	0.087 (3)
C131	-0.6330 (4)	0.7202 (3)	0.4887 (2)	0.044 (2)
C132	-0.6434 (4)	0.6529 (3)	0.4279 (2)	0.055 (2)
C133	-0.7474 (5)	0.6878 (4)	0.3527 (2)	0.068 (3)
C134	-0.8394 (5)	0.7889 (4)	0.3379 (2)	0.070 (3)
C135	-0.8301 (5)	0.8564 (3)	0.3966 (3)	0.070 (3)
C136	-0.7264 (5)	0.8223 (3)	0.4727 (2)	0.059 (2)

R = 0.044 and R_w 9) = 0.036, respectively. The residual electron density was calculated to be $\leq 0.16\,e/\text{Å}^3$. Interatomic distances, angles, and atomic fractional coordinates are included in Tables 1 and 2. Further crystal structure data have been deposited at Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen, FRG. Inquiries should be accompanied by the depository number CSD-55159, the names of the authors, and the full literature reference.

CAS Registry Numbers

1: 117953-66-9 / **2a**: 102862-11-3 / **2b**: 75540-68-0 / **3**: 542-92-7 / **4a**: 133399-76-5 / **4b**: 133399-77-6 / 5-isopropylidene-1,3-cyclopentadiene: 2175-91-9 / 2,3-dimethyl-1,3-butadiene: 513-81-5 / 5-isopropyl-4-phenyl-1,2,3-thiadiazole: 72770-67-3

1) W. T. Brady, *Tetrahedron* **37** (1981) 2949.
2) E. Schaumann, S. Scheiblich, *Tetrahedron Lett.* **26** (1985) 5269.
3) T. Lund, E.-A. Laifa, A. Senning, *Sulfur Lett.* **7** (1988) 103.
4) G. Seybold, Ch. Heibl, *Chem. Ber.* **110** (1977) 1225.
5) E. Schaumann, *Tetrahedron* **44** (1988) 1827.
6) E. Schaumann, J. Ehlers, H. Mrotzek, *Liebigs Ann. Chem.* **1979**, 1734.
7) G. Germain, P. Main, M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27** (1971) 368.
8) G. Sheldrick, Programs for Structure Determination, Univ. Cambridge 1977.
9) $w = \sigma F_o^{-2}$.

[69/91]