Heterocyclic Carbenes

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[1,3]Dithian-2-ylidene**

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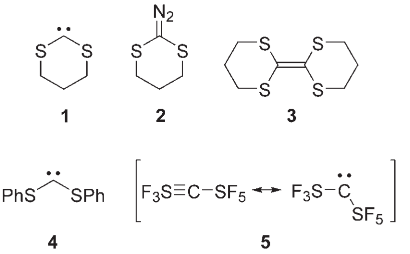
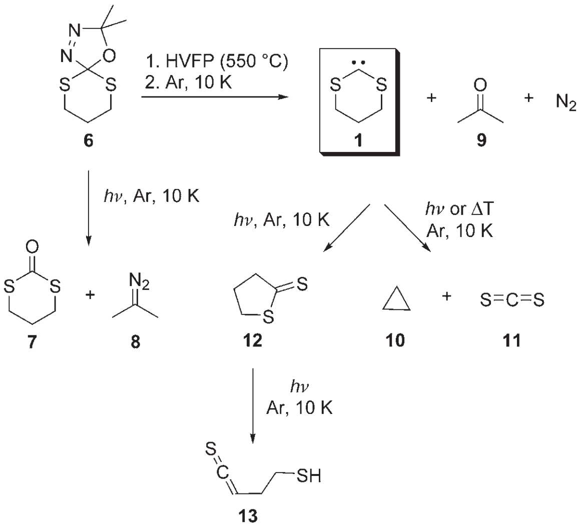
Dedicated to Professor Dieter Seebach

While many 1,3-heterocarbenes (RX-C-XR) substituted with X = N,N/N,O/N,S/P,Si/P,P and others have been well characterized and proven to be far more stable than anticipated, dithioalkyl carbenes, such as title compound **1**, are practically unknown.[1] Bisalkylthiocarbenes were suggested as reaction intermediates in the reactions of the respective orthothioformiates with a strong base[2] and in the decomposition of *p*-toluenesulfonylhydrazone salts.[3,4] The difficulty of the preparation of **1** and related dithiocarbenes is the unavailability of the respective diazo precursors. Even trapping of hitherto unobserved 2-diazodithiane (**2**) proved difficult as the product mixtures from the reactions with various electrophilic olefins were dominated by the formal carbene dimer of **1**, bis(1,3-dithianylidene) (**3**).[5] This class of tetrathioethylene[6] is quite important for various electronic applications, but they could alternatively form from the reactions of the carbene intermediates with the respective precursor carbanions.[7] The intermediacy of **4** in the equilibrium with tris(phenylthio)-methyl lithium was inferred from the observed typical carbene trapping reactions[8] and from kinetic measurements of the decomposition of the carbenoid in solution.[9] Probably the closest one has come to a spectroscopically identifiable dithiocarbene is with λ^6-sulfaacetylene **5**, which can be formally depicted as a zwitterion or a λ^3-sulfinylcarbene (Scheme 1).[10]

Important synthetic advances were made by generating dithiocarbenes from bis(alkylsulfanyl)oxadiazoline whose thermal decompositions and reactions with suitable electrophiles gave the formal carbene adducts (namely, dithioacetals) in good yields.[11–13] However, the free carbenes could not be characterized. Another reason for the unavailability of dithiocarbenes is the much lower π-donor ability[14] of sulfur relative to nitrogen for the stabilization of the carbene center (see below). As the dialkylthiooxadiazoline route apparently proved successful for the generation of dithiocarbene intermediates, we prepared known derivative **6**[13] (3,4-diaza-2,2-dimethyl-1-oxa-6,10-dithiaspiro[4.5]dec-3-ene; Scheme 2) to study its thermal and photochemical decomposition under matrix isolation conditions. This synthesis builds on the successful preparation of dioxycarbene precursors.[15]



Scheme 1. Title compound **1**, its diazo precursor **2**, dimerization product **3**, bis(phenylthio)carbene **4** (not observed), and sulfaacetylene **5** with its carbene resonance form.



Scheme 2. Photochemical and thermal decomposition of **6**, and photochemical reactions of **1**.

Compound **6**, which is, in contrast to earlier reports,[13] stable at room temperature, indeed shows the decomposition behavior we had hoped for (Scheme 2). Remarkably, the photochemical and thermal decomposition reactions of **6** are entirely different and complementary. Irradiation (λ_{max} = 313 nm) of **6** did not give **1** but instead gave 1,3-dithiane-2-on (**7**) and 2-diazopropane (**8**), as evident from comparisons with authentic samples and from the agreement with the DFT-computed vibrational frequencies. Carbene **1** was generated thermally through high-vacuum flash pyrolysis (HVFP) in a quartz tube at 550 °C and was trapped in an argon matrix at 10 K.

Carbene **1** shows strong absorption bands at 278 and 220 nm and a very weak band at around 390 nm (Figure 1).

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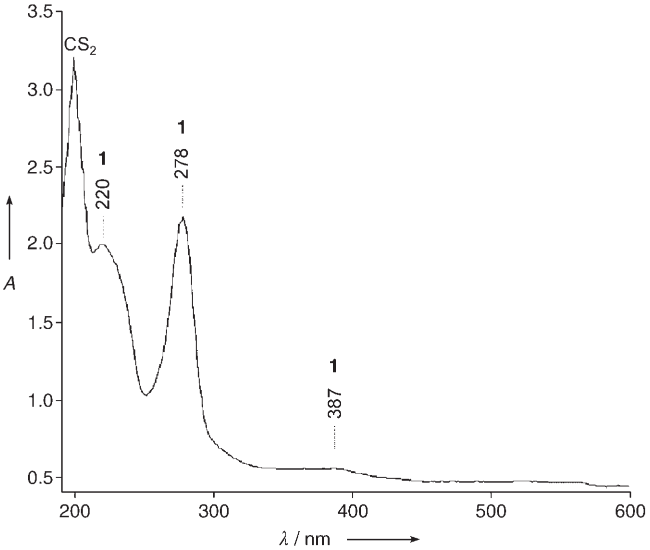


Figure 1. UV spectrum of carbene **1** at 10 K (Ar matrix).

The long-wavelength absorption stems from the HOMO–LUMO transition, whereas the intense absorptions originate from combinations of excitations. Irradiation of the matrix with wavelengths $\lambda > 385$, 280, and 254 nm leads to complete disappearance of the observed UV bands. The IR absorptions (Figure 2) parallel these findings and also vanish completely upon irradiation at the above wavelengths. IR spectra before and after irradiation allow the assignment of the IR bands of **1**. To evaluate the magnitude of matrix effects on the vibrational frequencies, we also generated **1** in an N_2 matrix for comparison (Table 1); the differences are rather small. The IR absorptions also agree very well with the computations at B3LYP and MP2 with a 6-311+G(d,p) basis set (unscaled). The intense symmetric and asymmetric S-C-S bond vibrations at 1011.8 and 664.7 cm^{-1} are particularly indicative of carbene **1**. The C_s optimized geometry (we use the B3LYP geometry for our discussion; the MP2 structure is very similar (see the Supporting Information)) indicates a short S^1–C^2 (=S^3–C^2) bond length of 1.665 Å (∢S-C-S = 126.3°) as opposed to the S^1–C^6 (=S^3–C^4) bond length of 1.870 Å; the S–C^2 (=S–C^2) bond length in dithiane is 1.827 Å (∢S-C-S = 115.4°). A comparison with the C=S bond length in CS$_2$ of 1.560 Å reveals that the double-bond character between the carbene center and the sulfur π-donor atoms is significant (see below).

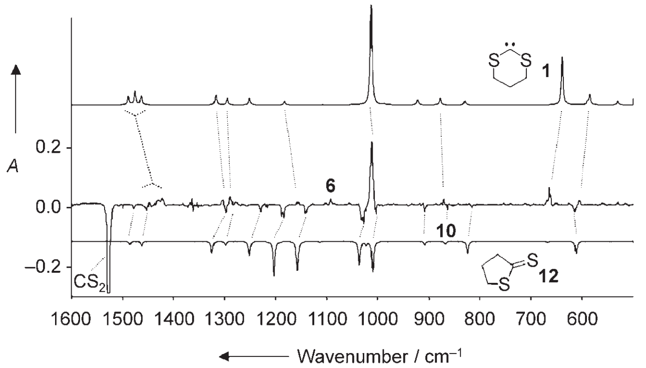


Figure 2. IR spectra of carbene **1** and dithiolactone **12** at 10 K (Ar matrix). The experimental difference spectrum is in the middle and the computed (B3LYP/6-311+G(d,p)) spectra above (for **1**) and below (for **12**).

Table 1: Measured and computed (unscaled) IR absorption frequencies of **1**.

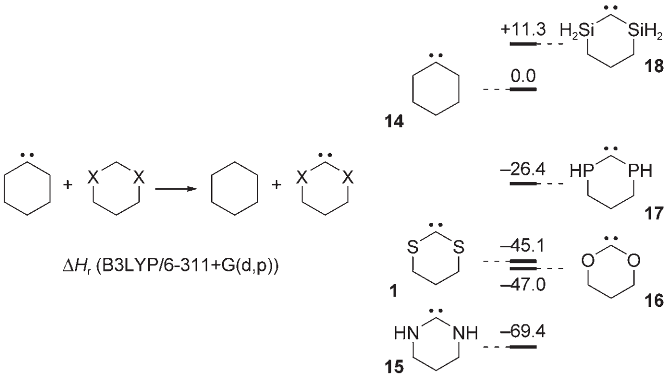
Symm., type[a]	Position [cm^{-1}] (Intensity [km mol^{-1}])			
	Computation, 6-311+G(d,p)		Experiment	
	MP2	B3LYP	Ar matrix	N_2 matrix
a'', rd	120.1 (0.0)	129.8 (0.0)		
a', rd	287.6 (4.9)	265.4 (3.9)		
a'', rd	349.1 (1.9)	347.2 (2.3)		
a', rd	386.4 (3.1)	367.7 (2.4)		
a', rd	392.5 (3.3)	380.1 (2.4)		
a', rd	549.5 (2.0)	530.1 (2.7)		
a', CS-ss	638.1 (8.0)	584.9 (6.7)	606.8 (w)	607.7 (w)
a'', CS-as	657.3 (1.3)	590.0 (2.2)		
a', SCS-ss	683.3 (33.3)	638.9 (31.2)	664.7 (m)	665.3 (m)
a'', CH$_2$-r	840.8 (1.5)	829.7 (2.4)		
a', CCC-s	907.5 (6.2)	878.1 (4.3)	879.7 (w)	872.3 (w)
a', CCC-s	949.2 (1.0)	922.3 (3.2)		
a', CH$_2$-r	1016.8 (0.4)	987.7 (0.6)		
a'', SCS-as	1056.0 (122.1)	1013.3 (64.5)	1011.8 (s)	1008.8 (s)
a'', CCC-s	1089.0 (3.3)	1049.0 (0.3)		
a'', CH$_2$-t	1134.7 (0.1)	1107.7 (0.2)		
a'', CH$_2$-t	1203.8 (0.9)	1182.8 (2.3)		
a', CH$_2$-t	1272.5 (4.5)	1251.4 (4.2)		
a', CH$_2$-w	1334.5 (4.3)	1295.1 (4.1)	1288.9 (w)	1290.1 (w)
a'', CH$_2$-w	1342.2 (8.7)	1317.4 (6.3)	1302.7 (w)	
a'', CH$_2$-w	1393.2 (0.0)	1380.0 (0.0)		
a'', CH$_2$-sc	1466.8 (3.6)	1463.6 (5.5)		
a', CH$_2$-sc	1479.9 (9.3)	1475.8 (8.8)	1422.4 (w)	
a', CH$_2$-sc	1497.3 (5.0)	1488.7 (5.5)		
a', CH-s	3074.9 (18.9)	3020.7 (25.2)		
a'', CH-s	3085.7 (11.9)	3044.8 (7.7)		
a', CH-s	3086.5 (16.3)	3046.8 (12.4)		
a', CH-s	3128.3 (12.1)	3062.7 (26.9)		
a'', CH-s	3152.1 (4.7)	3100.6 (6.8)		
a', CH-s	3156.1 (12.4)	3104.4 (18.4)		

[a] rd = ring deformation; ss/as = symmetric/asymmetric stretch; r = rocking; t = twisting; w = wagging; sc = scissoring; s = stretch.

Irradiation of **1** leads both to CS$_2$ and cyclopropane (**10**), which are also the main products from pyrolysis at 700 °C. These products are in line with the earlier findings that both the five-membered ring analogue of **6**[13] and the respective tosylhydrazone sodium salt[4] readily gave ethylene and the remaining stable fragments. Hence, this CS$_2$ extrusion reaction may also be viewed as the dithio analogue of the well known Corey–Winter method for the preparation of olefins from vicinal diols through the reaction with thiophosgen and phospane-induced loss of CO$_2$.[16] Formal thio-Wolff rearrangement of **1** gives dithiolactone **12**, which rearranges upon irradiation at 300 nm probably to thioketene **13** (IR absorption at 1772 cm^{-1}).

We examined the reactivity of **1** by condensing the pyrolysis products on a cooling finger without a stabilizing matrix at 80 K. We found that upon warming **1** is perfectly stable up to 100 K, whereas, at 120 K the UV and IR bands slowly decrease ($t_{1/2} \approx 45$ min) and disappear completely after

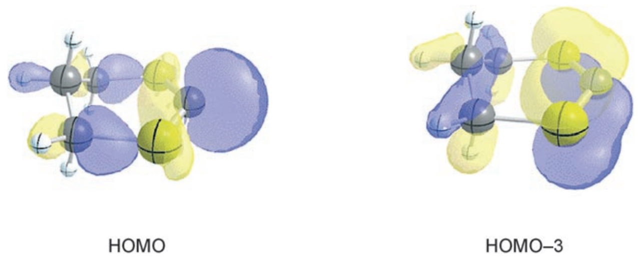
17 h. Upon warming to room temperature, we identified the known dimer[6] **3** by GC–MS. The stability of **1** relative to cyclohexenylidene (**14**) and several heterocarbenes (**15**–**18**) can also be estimated by the homodesmotic equation depicted in Scheme 3. As expected, nitrogen is the best π donor,[14] thus making **15** by far the most stable carbene in this series. Although surprising at first glance, the energy difference between dioxocarbene **16** and dithiocarbene **1** is negligible (1.9 kcal mol^{-1}), but this is in line with the findings for oxo- and thio-substituted carbenium ions that also are similarly stabilized by these heteroatoms.[17] This finding is striking because the difference in the stabilization between dinitrogen- and diphosphorous-substituted 1,3-heterocarbenes **15** and **17**, respectively, is very large (43.0 kcal mol^{-1}). Saturated disilacarbene **18** is actually destabilized relative to cyclohexenylidene **14** owing to the less effective hyperconjugation of Si–H versus C–H and the appreciable σ-donor character of the electropositive silicon atom.



Scheme 3. Stabilization enthalpies of 1,3-diheteroo-2-ylidenes.

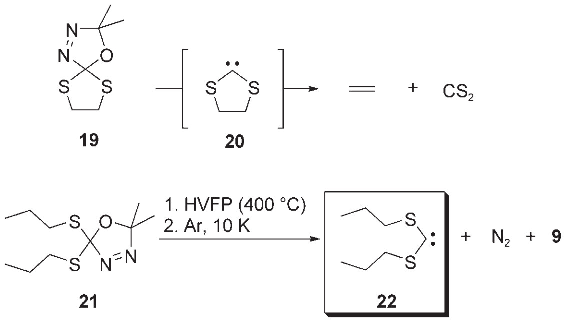
As for the other six-membered heterocarbenes, the electronic structure of **1** is characterized by several high-lying orbitals that describe the sp^2-type lone pair of electrons (HOMO) on the carbon atom and highly delocalized π-type MOs, such as HOMO-3 (Figure 3), which emphasizes the stabilizing power of the heteroatoms. As a consequence, the triplet state is far above the singlet ($\Delta E_{ST} = -33.8$ kcal mol^{-1} at B3LYP/6-311 + G(d,p)) and dithiocarbenes are expected to behave as nucleophiles.

We also attempted the preparation of the corresponding five-membered cyclic dithiocarbene **20** (Scheme 4), but noticed, in agreement with earlier findings, that the precursor **19**[13] is far more labile than **6**. Thermal treatment of **19** and co-condensation on an Ar matrix as before at 10 K only showed IR signals that correspond to ethylene and CS$_2$. The Corey–Winter-type CS$_2$ extrusion reaction apparently is quite facile for these small cyclic dithiocarbenes, so we turned our attention to the preparation of an di-*n*-alkyldithiocarbene that should not readily decompose into CS$_2$ and two alkyl fragments. Following the same protocol, the preparation of **21** was straightforward (Scheme 4).[11] Indeed, HVFP and co-condensation of the pyrolysis products on an Ar matrix gives the novel di-*n*-propyldithiocarbene **22**.



HOMO HOMO–3

Figure 3. Selected high-lying molecular orbitals (B3LYP/6-311+G(d,p)) of carbene **1**; sulfur atoms in yellow, carbon atoms in black.



Scheme 4. Other dialkyl dithiocarbenes and their precursors.

As with **1**, carbene **22** can be identified by comparison of experimental and computed IR absorptions (Figure 4) and by the strong band observed at 300 nm in the UV spectrum. The IR spectra of **1** and **22** compare well and both show a characteristic absorption just above 1000 cm^{-1} (**22** = 1039.9 cm^{-1}). Irradiation of **22** with $\lambda = 313$ nm for 17 min leads to its disappearance and generation of CS; hence, the decomposition path is different from that of **1** (see above).

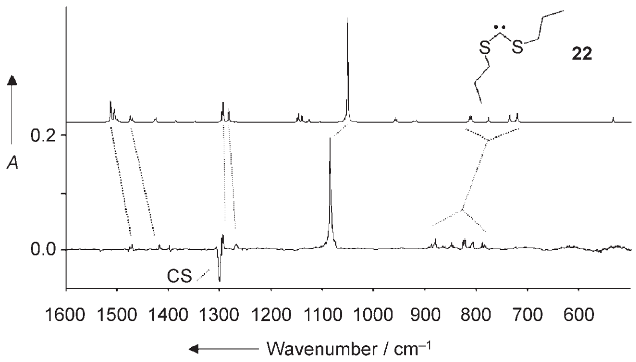


Figure 4. IR spectra of carbene **22** and CS at 10 K (Ar matrix): experimental-difference spectrum (bottom) versus the computed (B3LYP/6-311 + G(d,p)) spectrum above (for *cis*,*trans*-**22**).

In summary, we have presented the first experimental IR and UV spectroscopic characterization of two dithiocarbenes, dithianylidene **1** and di-*n*-propyldithiocarbene **22**, generated thermally from the respective dialkylthiooxadiazoline precursors. Carbene **1** is considerably less stable than the exceptionally stable nitrogen-substituted analogues and dimerizes at temperatures above 100 K; its stability is comparable to that of the dioxo analogue. The photochemistry of **1** is interesting, as it formally represents the dithiophotochemical variation of the practical Corey–Winter reaction.

Experimental Section

Matrix isolation experiments.: Compounds **6**, **19**, and **21** were subjected to HVFP at 400–700 °C (empty quartz tube, inner diameter: 8 mm, length of heating zone: 50 mm). The products thus formed were trapped immediately thereafter on a cold (10 K) CsI (or BaF_2) window together with a large excess of Ar or N_2. These matrices were examined with FT-IR and UV/Vis spectroscopy. The spectra and additional information are collected in the Suppporting Information.

Computations: Geometries were fully optimized at the B3LYP[18] and MP2[19] levels of theory with a 6-311+G(d,p) basis set including frequency analyses to disclose the nature of all stationary points (Nimag = 0 for minima and 1 for transition structures). All computations utilized the Gaussian03 program package.[20] The *xyz* coordinates and the energies of all computed species are collected in the Supporting Information.

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Keywords: computational chemistry · dialkyldithiocarbenes · dithianes · matrix isolation · sulfur

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