

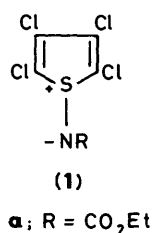
Interaction of Thiophene S,N-Ylides with Dimethyl Acetylenedicarboxylate

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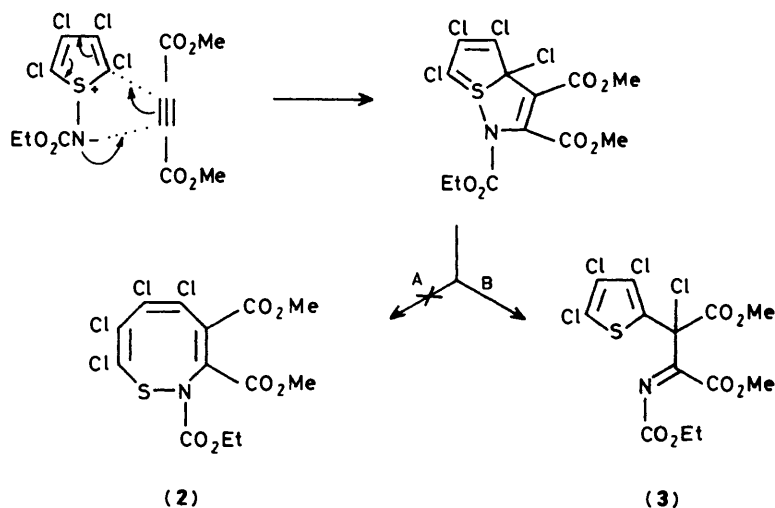
The title reaction yields two products, dimethyl tetrachlorophthalate, by [4 + 2] cycloaddition and dimethyl 2-chloro-3-ethoxycarbonylimino-2-trichloro-2-thienylsuccinate by [6 + 2] cycloaddition. The latter structure, verified by X-ray crystallography, corrects an earlier report.

We recently noted that tetrachlorothiophene reacts with reactive nitrenes such as ethoxycarbonylnitrene to give stable S,N-ylides (1).¹ Other thiophenes react similarly to give



four aliphatic ester absorptions and only eight *sp*² resonances, presumably one signal being overlapped. A more careful scrutiny revealed a weak quaternary aliphatic resonance at 66.15 p.p.m. as required by structure (3), the long relaxation time of this carbon precluding its ready observation.

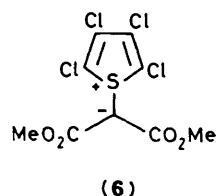
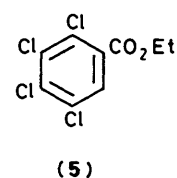
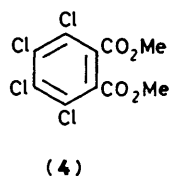
Tetrachlorothiophene dioxide, a diene of related reactivity, showed no evidence for any reaction with the same acetylene after one week of heating at 80 °C in cyclohexane. Under these conditions we obtained two products from the ylide (1a): (i) dimethyl tetrachlorophthalate (4) (36%) by the expected [4 + 2] addition of the ylide to the acetylene followed by extrusion of ethyl thionitrosoformate; (ii) dimethyl 2-chloro-3-ethoxy-



Scheme.

transient, trappable ylides.² These ylides (1) react as electron-deficient Diels–Alder dienes with dienophiles and as dienophiles with electron-rich dienes.³ We also observed that the ylide (1a) reacted slowly with dimethyl acetylenedicarboxylate, a reaction which we interpreted as a [6 + 2] cycloaddition to give compound (2) (Scheme, path A).³ We now show that while this mode of cycloaddition is correct the subsequent rearrangement involves an S,N-bond cleavage and 1,2-chlorine shift to yield (3) (path B) rather than an S,C-bond breaking as in path A. The structure of the product (3) has been verified by X-ray crystallography and corroborated by other spectroscopic data.

In our earlier publication³ we observed that analytical and infrared, mass spectral and ¹H n.m.r. data were consistent with the structure (2). Also that ¹³C n.m.r. spectroscopy revealed



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Table 1. Crystallographic data

Formula	C ₁₃ H ₁₁ Cl ₄ NO ₆ S
Space group	P2 ₁ /c
M _r /g mol ⁻¹	451.10
a/Å	12.208(2)
b/Å	10.413(1)
c/Å	14.849(1)
β/°	104.97(1)
V/Å ³	1 823.5
Z	4
F(000)	912
D _c /g cm ⁻³	1.64
μ(Mo-K _α)/cm ⁻¹	7.9
Reflections measured	5 577
Reflections used (>σ)	3 890
Variables refined	260
$R_w = \frac{\sum w \Delta }{\sum w F_o }$	0.025
$R = \frac{\sum \Delta F }{\sum F_o }$	0.058

Table 2. Fractional co-ordinates (× 10⁴, × 10⁵ for S and Cl, × 10³ for H)

	x/a	y/b	z/c
S(1)	3 788(6)	17 915(6)	88 279(4)
C(2)	1 381(2)	2 325(2)	9 810(2)
C(3)	1 429(2)	3 620(2)	9 823(2)
C(4)	674(2)	4 216(2)	9 045(2)
C(5)	60(2)	3 338(2)	8 465(2)
C(6)	2 074(2)	1 414(2)	10 519(1)
C(7)	3 344(2)	1 744(2)	10 744(2)
N(8)	3 851(2)	2 179(2)	11 528(1)
C(9)	5 007(2)	2 553(3)	11 767(2)
O(10)	5 089(1)	3 731(2)	11 473(1)
C(11)	6 234(3)	4 295(4)	11 741(3)
C(12)	6 185(4)	5 494(4)	11 225(3)
O(13)	5 735(2)	1 923(2)	12 266(1)
C(14)	3 938(2)	1 518(2)	9 976(2)
O(15)	3 211(1)	1 146(2)	9 200(1)
C(16)	3 651(3)	883(3)	8 396(2)
O(17)	4 931(2)	1 619(2)	10 099(1)
C(18)	1 911(2)	-11(2)	10 233(2)
O(19)	2 768(1)	-691(2)	10 744(1)
C(20)	2 708(3)	-2 083(3)	10 578(2)
O(21)	1 125(1)	-425(2)	9 663(1)
Cl(22)	15 891(5)	15 010(6)	115 694(4)
Cl(23)	22 589(6)	45 440(6)	106 969(5)
Cl(24)	5 755(7)	58 380(7)	88 643(5)
Cl(25)	-9 558(6)	36 320(7)	74 589(5)
H(11A)	641(3)	442(3)	1 237(2)
H(11B)	673(3)	381(3)	140(2)
H(12A)	699(3)	602(3)	1 141(2)
H(12B)	605(3)	527(3)	1 052(2)
H(12C)	565(3)	591(4)	144(3)
H(16A)	306(3)	101(4)	790(2)
H(16B)	388(3)	5(3)	843(2)
H(16C)	410(3)	158(3)	837(2)
H(20A)	198(3)	-236(3)	1 066(2)
H(20B)	266(3)	-219(3)	991(2)
H(20C)	331(3)	-242(3)	1 097(2)

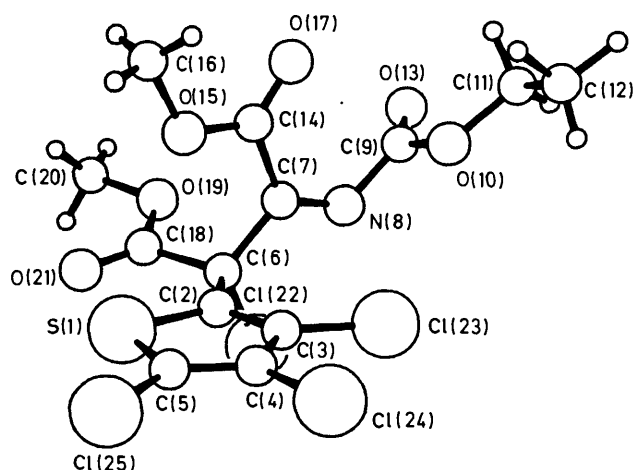
carbonylimino-2-trichlorothien-2-ylsuccinate (**3**) (38%) which crystallised as rhombs from hexane. The two products were readily separated by flash chromatography. The same glide (**1a**) reacted more rapidly with ethyl propiolate to give solely the known⁴ [4 + 2] adduct (**5**) in high yield, but was unreactive towards acetonitrile. Furthermore, the related S₂C-ylide (**6**) reacted slowly (8 days) with dimethyl acetylenedicarboxylate in

Table 3. Bond lengths (Å)

S(1)-C(2)	1.735(2)	S(1)-C(5)	1.710(2)
C(2)-C(3)	1.349(3)	C(2)-C(6)	1.505(3)
C(3)-C(4)	1.420(3)	C(3)-Cl(23)	1.720(2)
C(4)-C(5)	1.344(3)	C(4)-Cl(24)	1.710(2)
C(5)-Cl(25)	1.705(2)	C(6)-C(7)	1.539(3)
C(6)-C(18)	1.542(3)	C(6)-Cl(22)	1.808(2)
C(7)-N(8)	1.253(2)	C(7)-C(14)	1.519(3)
N(8)-C(9)	1.417(3)	C(9)-O(10)	1.315(3)
C(9)-O(13)	1.194(3)	O(10)-C(11)	1.473(3)
C(11)-C(12)	1.458(5)	C(14)-O(15)	1.317(2)
C(14)-O(17)	1.186(3)	O(15)-C(16)	1.456(3)
C(18)-O(19)	1.327(2)	C(18)-O(21)	1.185(2)
O(19)-C(20)	1.469(3)		

Table 4. Valence angles (°)

C(2)-S(1)-C(5)	91.0(1)	S(1)-C(2)-C(3)	110.5(2)
S(1)-C(2)-C(6)	122.2(2)	C(3)-C(2)-C(6)	127.3(2)
C(2)-C(3)-C(4)	114.1(2)	C(2)-C(3)-Cl(23)	125.8(2)
C(4)-C(3)-Cl(23)	120.1(2)	C(3)-C(4)-C(5)	111.2(2)
C(3)-C(4)-Cl(24)	124.3(2)	C(5)-C(4)-Cl(24)	124.5(2)
S(1)-C(5)-C(4)	113.3(2)	S(1)-C(5)-Cl(25)	120.0(2)
C(4)-C(5)-Cl(25)	126.8(2)	C(2)-C(6)-C(7)	111.3(2)
C(2)-C(6)-C(18)	113.9(2)	C(7)-C(6)-C(18)	109.0(2)
C(2)-C(6)-Cl(22)	108.8(2)	C(7)-C(6)-Cl(22)	109.7(1)
C(18)-C(6)-Cl(22)	103.8(1)	C(6)-C(7)-N(8)	120.7(2)
C(6)-C(7)-C(14)	116.9(2)	N(8)-C(7)-C(14)	122.5(2)
C(7)-N(8)-C(9)	123.6(2)	N(8)-C(9)-O(10)	109.2(2)
N(8)-C(9)-O(13)	122.5(3)	O(10)-C(9)-O(13)	127.6(3)
C(9)-O(10)-C(11)	115.5(2)	O(10)-C(11)-C(12)	107.0(3)
C(7)-C(14)-O(15)	111.0(2)	C(7)-C(14)-O(17)	122.3(2)
O(15)-C(14)-O(17)	126.7(2)	C(14)-O(15)-C(16)	117.6(2)
C(6)-C(18)-O(19)	109.2(2)	C(6)-C(18)-O(21)	124.7(2)
O(19)-C(18)-O(21)	126.0(2)	C(18)-O(19)-C(20)	115.7(2)

Figure 1. Perspective view of molecule (**3**) with atomic numbering

refluxing benzene to yield solely tetrachlorothiophene (88%) as recognisable product, most of the acetylene being recovered.

X-Ray Crystallography.—Diffraction intensities were measured at 20 °C with an Enraf-Nonius CAD4 diffractometer, using graphite monochromated Mo radiation, $\lambda(\text{Mo-K}\alpha) = 0.71073 \text{ \AA}$. A pure ω -scan was used, the angle changed by $0.53 + 0.35 \tan \theta$ (degrees). The horizontal aperture was fixed to 1.3 mm, the vertical slit to 4 mm. A variable scan speed was

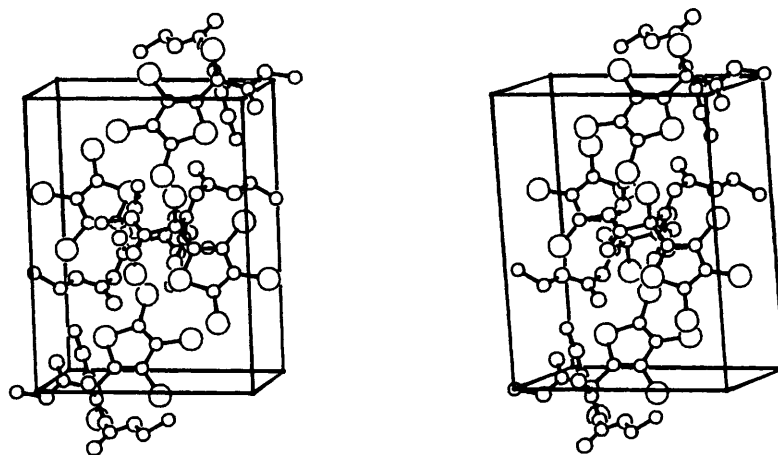


Figure 2. Stereoscopic drawing of the unit cell

employed with a maximum of $5.49^\circ/\text{min}$ and a minimum corresponding to 50 s measuring time per reflection.

The unit cell and the orientation matrix were determined using 25 reflections in the range $6\text{--}18^\circ$ in θ . Crystal stability was tested every hour (loss 0.6%), and the orientation every 200 reflections. A new orientation matrix was determined if the settings of one of the test reflections deviated more than 0.09° from its original value.

Data were corrected for Lorentz and polarisation effects, and for absorption with an empirical correction method involving psi-scans.⁵ The structure was solved routinely with MULTAN80⁶ and refined anisotropically with SHELX76⁷ using a full matrix method with σ_F^2 -weights. All hydrogen atoms were located from subsequent Fourier-maps, and refined with a common isotropic temperature factor, $U = 0.148 \pm 0.004 \text{ \AA}^2$.

Relevant crystallographic data are summarised in Table 1. Fractional co-ordinates, bond lengths, and valence angles appear in Tables 2–4. Figure 1 is a perspective drawing of the molecule, showing the numbering scheme used, and Figure 2 is a stereopicture of the unit cell.

Tables of thermal parameters, bond lengths and valence angles involving hydrogen atoms, and lists of observed and

calculated structure factors are available on request from the Reference Section, CSIR Library Division, NII, PO Box 395, Pretoria 0001.

References

- 1 O. Meth-Cohn and G. van Vuuren, *J. Chem. Soc., Chem. Commun.*, 1984, 190.
- 2 O. Meth-Cohn and G. van Vuuren, *Tetrahedron Lett.*, 1986, **27**, 1105.
- 3 O. Meth-Cohn and G. van Vuuren, *J. Chem. Soc., Perkin Trans. 1*, 1986, 233.
- 4 'Dictionary of Organic Compounds,' Chapman and Hall, New York, 5th edn., 1982, vol. 5, p. 5141.
- 5 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr., Sect. A*, 1968, **24**, 351.
- 6 P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woolfson, 'MULTAN80, A System of Computer Programs for the Automatic Solution of Structures from X-Ray Diffraction Data,' Universities of York (England) and Louvain (Belgium), 1980.
- 7 G. M. Sheldrick, 'SHELX76, A Program for Crystal Structure Determination,' University of Cambridge, England, 1976.

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