Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Unexpected formation of a thiazolo[3,2-*a*]-pyridinium methide: a novel subclass of mesoionic compounds

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.077
Data-to-parameter ratio = 17.5

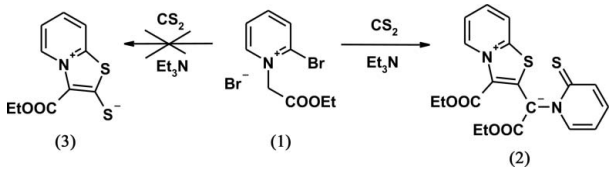
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 17 February 2006
Accepted 27 March 2006.

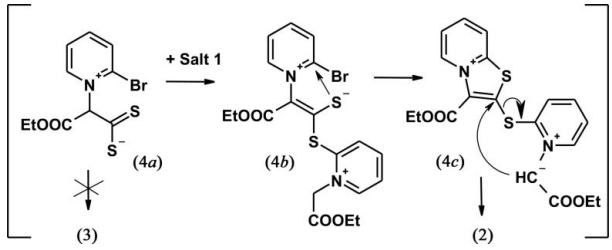
While trying to prepare mesoionic thiazolo[3,2-*a*]pyridinium-2-thiolate by reaction of 2-bromo-1-(ethoxycarbonylmethyl)pyridinium bromide with CS_2, an unexpected product was formed, namely (ethoxycarbonyl)[3-(ethoxycarbonyl)-1,3-thiazolo[3,2-*a*]pyridin-4-ium-2-yl](2-thioxo-1,2-dihydropyridin-1-yl)methanide, $C_{19}H_{18}N_2O_4S_2$. The structure of the product corresponds to a previously unknown subclass of mesoionic thiazolo[3,2-*a*]pyridinium-2-methylides.

Comment

We have previously described the successful synthesis of previously unknown mesoionic thiazolo[3,2-*a*]pyridinium-2-thiolates by the reaction of 2-halogen-*N*-phenacylpyridinium salts with CS_2 (Babaev *et al.*, 2004). An analogous reaction between 2-bromo-1-(2-ethoxy-2-oxoethyl)pyridinium bromide and CS_2 unexpectedly formed the title compound, (2), instead of the desired thiolate, (3) (see first scheme below).



The structure of (2) is shown in Fig. 1. The main structural feature of the molecule is the difference in the lengths of the two C—S bonds (C3—S4 and C5—S4) in the thiazole ring (Table 1). Additionally, the N1—C2 bond is longer than the other two C—N bonds of the bicyclic system. These observations may reflect the separation of charges in the mesoionic system into two parts: a positively charged 2-thiopyridinium fragment and a negatively charged C2—C3—C10 unit. Interestingly, the ester groups C11═O11 and C15═O15 seem to make a smaller contribution to the delocalization of the negative charge, since the C10—C11 and C2—C15 distances are relatively long.



A possible rationalization of the formation of (2) is shown in the second scheme. Initial reaction of CS_2 with the ylide

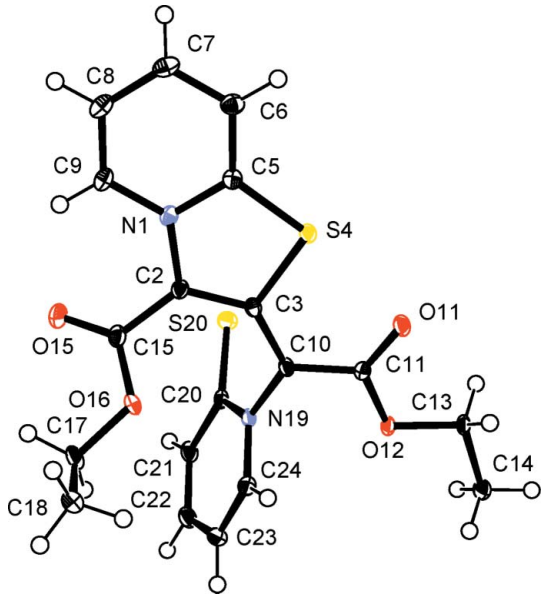


Figure 1
The structure of (2), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level, with H atoms shown as spheres of arbitrary radius.

from (1) leads to the formation of the adduct (4*a*). This could react with an additional molecule of (1) to give the intermediate (4*b*) and then (4*c*). The arylthio-group in (4*c*) could then undergo intramolecular substitution leading to the product (2). Substitution of an *SR* group in analogous 2-*RS*-thiazolo[3,2-*a*]isoquinolinium salts in the presence of CH acids is well documented (Mizuyama *et al.*, 1976).

Experimental

2-Bromo-1-(2-ethoxy-2-oxoethyl)pyridinium bromide, (1) (9.8 g, 30 mmol), was suspended in dichloromethane (70 ml). The mixture was cooled to 233 K and Et_3N (13.9 ml, 10.1 g, 100 mmol, 3.3 equivalents) added dropwise. The resulting suspension was kept at 233 K for an additional 15 min and then CS_2 (7.25 ml, 9.12 g, 120 mmol, 4 equivalents) was added. The reaction mixture turned yellow, then deep red as the temperature was increased to 283 K. After standing overnight, the mixture was diluted with water (200–300 ml), the organic layer separated and the aqueous layer extracted with dichloromethane (2 × 200 ml). The organic phases were combined, dried (Na_2SO_4) and evaporated. The resulting dark residue was dissolved in chloroform and purified using flash chromatography (SiO_2, $CHCl_3$). A crude dark-brown solid (2.45 g) was obtained, which yielded dark-red crystals of (2) (2.1 g, 34%, m.p. 463–466 K) after final recrystallization from acetone.

Crystal data

$C_{19}H_{18}N_2O_4S_2$
M_r = 402.47
Triclinic, $P\overline{1}$
a = 6.8600 (14) Å
b = 9.0710 (18) Å
c = 14.634 (3) Å
α = 82.66 (3)°
β = 80.06 (3)°
γ = 84.11 (3)°
V = 886.6 (3) Å^3
Z = 2
D_x = 1.508 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6851 reflections
θ = 3.5–31°
μ = 0.33 mm^{-1}
T = 100 (2) K
Plate, dark red
0.40 × 0.40 × 0.14 mm

Data collection

Stoe IPDS diffractometer
ω scans
Absorption correction: none
6851 measured reflections
4380 independent reflections
3810 reflections with $I > 2\sigma(I)$
R_{int} = 0.020
θ_{max} = 29.1°
$h = -8 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.032
$wR(F^2)$ = 0.077
S = 1.03
4308 reflections
246 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.5422P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 0.46 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C5	1.3677 (16)	C11—O12	1.3557 (15)
N1—C9	1.3758 (16)	O12—C13	1.4581 (14)
N1—C2	1.4143 (17)	C13—C14	1.5081 (18)
C2—C3	1.4082 (17)	C15—O15	1.2160 (17)
C2—C15	1.4636 (17)	C15—O16	1.3356 (18)
C3—C10	1.3928 (17)	O16—C17	1.4567 (16)
C3—S4	1.7675 (13)	C17—C18	1.504 (2)
S4—C5	1.7237 (14)	N19—C24	1.3717 (18)
C5—C6	1.3983 (18)	N19—C20	1.3852 (17)
C6—C7	1.3793 (19)	C20—C21	1.4268 (17)
C7—C8	1.395 (2)	C20—S20	1.6897 (15)
C8—C9	1.373 (2)	C21—C22	1.366 (2)
C10—C11	1.4337 (17)	C22—C23	1.406 (2)
C10—N19	1.4381 (15)	C23—C24	1.3626 (19)
C11—O11	1.2295 (15)		
C5—N1—C9	119.24 (11)	O11—C11—O12	122.22 (11)
C5—N1—C2	113.37 (11)	O11—C11—C10	122.90 (12)
C9—N1—C2	127.35 (11)	O12—C11—C10	114.87 (10)
C3—C2—N1	112.66 (11)	C11—O12—C13	114.42 (9)
C3—C2—C15	128.68 (12)	O12—C13—C14	107.74 (10)
N1—C2—C15	118.38 (11)	O15—C15—O16	124.07 (12)
C10—C3—C2	131.70 (11)	O15—C15—C2	124.55 (13)
C10—C3—S4	118.39 (9)	O16—C15—C2	111.28 (11)
C2—C3—S4	109.70 (9)	C15—O16—C17	118.33 (11)
C5—S4—C3	91.55 (7)	O16—C17—C18	107.97 (12)
N1—C5—C6	121.32 (12)	C24—N19—C20	122.52 (11)
N1—C5—S4	112.47 (10)	C24—N19—C10	116.97 (11)
C6—C5—S4	126.20 (10)	C20—N19—C10	120.35 (11)
C7—C6—C5	119.50 (12)	N19—C20—C21	115.31 (12)
C6—C7—C8	118.49 (13)	N19—C20—S20	122.81 (9)
C9—C8—C7	121.33 (13)	C21—C20—S20	121.88 (11)
C8—C9—N1	120.12 (12)	C22—C21—C20	122.31 (13)
C3—C10—C11	119.18 (11)	C21—C22—C23	119.75 (12)
C3—C10—N19	122.55 (11)	C24—C23—C22	118.59 (13)
C11—C10—N19	117.51 (11)	C23—C24—N19	121.43 (13)

All H atoms were refined using a riding model, with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for aromatic, C—H = 0.99 Å and U_{iso}(H) = 1.2U_{eq}(C) for CH_2, and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for CH_3 atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are indebted to the Russian Foundation for Basic Research for covering the licence fee for use of the Cambridge Structural Database (Version 5.27; Allen, 2002).

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