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3,3-Bis(methylthio)-2-oxo-*N*-phenylpropanamide

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.044
wR factor = 0.120
Data-to-parameter ratio = 13.9

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

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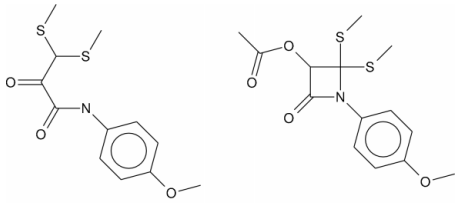
The title compound, $C_{12}H_{15}NO_3S_2$, is the result of a rearrangement of a bis(methylthio)-β-lactam after prolonged exposure to silica gel. The compound crystallizes with a single molecule in the asymmetric unit.

Comment

1,2,3-Vicinal tricarbonyl systems have been shown to serve as potent electrophiles in organic synthesis (Wasserman *et al.*, 1993; Wasserman *et al.*, 1999). In this paper we report the structure of a tricarbonyl system, (I), having the terminal carbonyl group as masked functionality, which was obtained from the rearrangement of 1-(4′-methoxy-phenyl)-3-acetoxy-4,4-bis(methylthio)azetidin-2-one (II) in quantitative yield. Note that, with regard to 'masked functionality', oxidation of (I) with oxidizing reagents such as $AgClO_4$ or $I_2/NaHCO_3$ would result in loss of S1—C1*A* and S2—C2*A* and formation of an aldehyde at C4, regenerating the 1,2,3-vicinal tricarbonyl system. Thus (I) could be described as a 1,2,3 tricarbonyl system with the terminal C-atom protected, or masked, by the two SMe groups.



Compound (II) was prepared by a known procedure (Sharma *et al.*, 1987). Rearrangement of (II) occurred when the bis(methylthio)-β-lactam was exposed to silica gel (in flash chromatography) for prolonged periods. Previously, it has been observed that 1-(4′-methoxy-phenyl)-3-acetoxy-4,4-bis-(methylthio)azetidin-2-one, upon hydrolysis with 1% NaOH in aqueous methanol, gives the 3-hydroxy derivative (Bari *et al.*, 1999). The latter was found to be unstable at room temperature and was slowly converted to a new compound with higher R_f than the 3-hydroxy derivative (Bari *et al.*, 1999). We feel that this unidentified product might be identical to the 1,2,3-tricarbonyl system reported in this paper. Studies toward this end are currently under way in our laboratory, as well as studies showing the utility of the aforementioned rearrangement in organic synthesis. It should be noted that monocyclic β-lactams related to (II) have been prepared and appear to be stable (Konaklieva, 2002; Deschamps *et al.*, 2003).

The title compound crystallizes in the monoclinic space group *C*2/*c* with one molecule in the asymmetric unit (Fig. 1). Routine structural checking indicates that the C2—C3 bond is

long [1.538 (2) Å] for a Csp^2—Csp^2 bond (Spek, 2001). A search of the Cambridge Structural Database (Allen, 2002) for all Csp^2—Csp^2 bonds yields an average length of 1.451 (43) Å. However, restricting the search to only those bonds involving two adjacent carbonyl group s flanked by C and N atoms yields an average bond length of 1.535 (21) Å, a value consistent with that observed in this study.

Experimental

The β-lactam 1-(4-methoxyphenyl)-3-acetoxy-4,4-bis(methylthio)-azetidin-2-one was prepared in our laboratories using the [2 + 2]-cycloaddition reation between acetoxyacetyl chloride and dithiocarbonimidate by a known procedure (Sharma *et al.*, 1987). The crude reaction mixture was then treated with 5% NH_4Cl. The aqueous layer was extracted with methylene chloride, and the combined organic layers were dried over anhydrous $MgSO_4$ and concentrated *in vacuo*. Flash chromotography using silica gel yielded 45% of pure 1-(4-methoxyphenyl)-3-acetoxy-4,4-bis(methylthio)-azetidin-2-one as an oil. Flash chromotography of the mixed fractions containing 1-(4-methoxyphenyl)-3-acetoxy-4,4-bis(methylthio)azetidin-2-one and a compound with a higher *Rf* than the β-lactam yielded the title compound in quantitative yield. Pale yellow crystals were grown by evaporation of a methylene chloride solution.

Crystal data

$C_{12}H_{15}NO_3S_2$	D_x = 1.384 Mg m^{-3}
M_r = 285.37	Cu $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2025 reflections
a = 29.7331 (5) Å	θ = 8.4–66.9°
b = 5.3499 (1) Å	μ = 3.54 mm^{-1}
c = 17.4428 (3) Å	T = 296 (2) K
β = 99.099 (1)°	Rod, pale yellow
V = 2739.7 (1) Å^3	0.70 × 0.16 × 0.07 mm
Z = 8	

Data collection

Bruker SMART 6000 CCD diffractometer	2328 independent reflections
	1977 reflections with $I > 2\sigma(I)$
ω scans	R_{int} = 0.049
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	θ_{max} = 67.1°
	$h = -33 \rightarrow 33$
T_{min} = 0.527, T_{max} = 0.776	$k = -6 \rightarrow 5$
8381 measured reflections	$l = -17 \rightarrow 20$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.081P)^2 + 0.0191P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.044	
$wR(F^2)$ = 0.120	
S = 1.05	$(\Delta/\sigma)_{max}$ = 0.003
2328 reflections	$\Delta\rho_{max}$ = 0.24 e Å^{-3}
168 parameters	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	Extinction correction: *SHELXL*
	Extinction coefficient: 0.0037 (3)

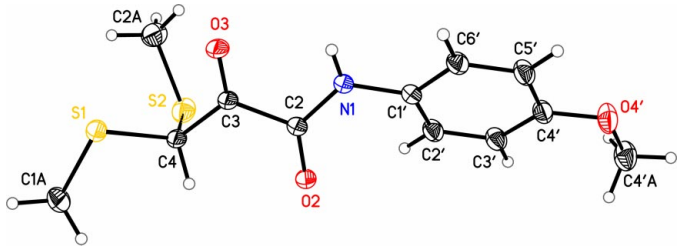


Figure 1
View of (I), showing the labeling of the non-H atoms. Displacement ellipsoids are shown at the 20% probability level.

The coordinates for H1 were refined, while its isotropic displacement parameter was set to 1.2U_{eq}(N1). All other H atoms were refined using a riding model.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000) and *XPREP* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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