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3-[(*Z*)-*p*-Chlorophenylthio-(*E*)-trimethylsilylmethylidene]-1,4-dimethyl-4-trimethylsilylazetidin-2-one: an α-Alkylidene-*β*-lactam

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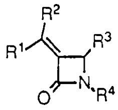
Abstract. $C_{18}H_{28}ClNOSSi_2$, $M_r = 398\cdot12$, triclinic, $P\bar{1}$, $a = 10\cdot943\,(3)$, $b = 13\cdot018\,(3)$, $c = 8\cdot074\,(1)$ Å, $\alpha = 76\cdot74\,(1)$, $\beta = 99\cdot04\,(2)$, $\gamma = 90\cdot27\,(2)°$, $V = 1105\cdot0\,(4)$ Å^3, $Z = 2$, $D_x = 1\cdot196$ g cm^{-3}, $\lambda(\text{Mo}\,K\alpha) = 0\cdot71069$ Å, $\mu(\text{Mo}\,K\alpha) = 3\cdot34$ cm^{-1}, $F(000) = 424$, $T = 295$ K, final $R = 0\cdot044$ for 2908 observed reflections. The *β*-lactam ring is approximately planar with none of its four atoms deviating by more than 0·018 (3) Å from their least-squares plane. The structure shows that 3-[(*Z*)-*p*-chlorophenylthio-(*E*)-trimethylsilylmethylidene]-4-methyl-4-trimethylsilylazetidin-2-one, which is formed by addition of chlorosulfonylisocyanate (CSI) to the allene $(Me)(Me_3Si)C^3{=}C^2{=}C^1(SiMe_3)(SC_6H_4Cl)$, results from CSI addition to the $C^2{=}C^3$ bond and not to the $C^1{=}C^2$ bond as found for several other closely related allenes.



(1)

Introduction. Several potent *β*-lactamase inhibitors possess the α-alkylidene-*β*-lactam subunit (1). Included in this class are the asparenomycins (Kawamura, Yasuda, Mayama & Tanaka, 1982), Ro15-1903 (Arisawa & Then, 1982) and 6-[(*Z*)-methoxymethylene]-penicillanic acid (Brenner, 1985). We have recently developed a strategy to prepare synthetically versatile members of this class *via* the addition of chlorosulfonylisocyanate, CSI, to functionalized allenes (Buynak, Pajouhesh, Lively & Ramalakshmi, 1984; Buynak, Rao, Pajouhesh, Chandrasekaran, Finn, de Meester & Chu, 1985; Buynak, Rao, Chandrasekaran, Haley, de Meester & Chu, 1985). The reaction of CSI with olefins is well documented (Rasmussen & Hassner, 1976). The 2 + 2 addition occurs in a stereo- and regiospecific fashion with the N atom bonding to that C atom bearing the highest degree of carbocation-

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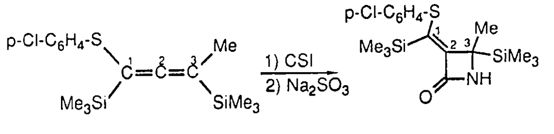
stabilizing substituents. While exploring the addition of CSI to the allenyl sulfides $(p\text{-ClC}_6\text{H}_4\text{S})R\text{C}^1{=}\text{C}^2{=}\text{C}^3\text{Me}_2$ and $(p\text{-ClC}_6\text{H}_4\text{S})(\text{Me}_3\text{Si})\text{C}^1{=}\text{C}^2{=}\text{C}^3R\text{Me}$ (where R = H or Me), we observed that the addition occurs to the $\text{C}^1{=}\text{C}^2$ bond with N becoming attached to the S-bearing C^1 atom. However, in the case of allene (2), regiospecificity was unexpectedly reversed with CSI adding to the $\text{C}^2{=}\text{C}^3$ bond to form (3) (Buynak, Rao, Chandrasekaran *et al.*, 1985). To confirm the structure of (3), we determined the structure of its *N*-methyl derivative which is reported here.



(2) (3)

Experimental. Crystals of the title compound are colorless prisms. Accurate unit-cell parameters obtained by least-squares refinement of 15 reflections in the range $21 < 2\theta < 28°$, space group $P\bar{1}$, crystal dimensions 0·66 × 0·39 × 0·15 mm. Automatic Syntex $P2_1$ diffractometer, graphite-monochromated Mo $K\alpha$ radiation, $\theta/2\theta$ scan mode, 3913 independent reflections collected in the range $3 < 2\theta < 50°$, hkl range h −12→12, k −14→15, l 0→9, 2908 observed reflections with $I > 3\sigma(I)$, $\sigma(I)$ from counting statistics. Three standard reflections remeasured after every 100 reflections showed no change in intensity greater than $2\sigma(I)$. Lorentz–polarization correction, no absorption or extinction corrections. The structure was solved by *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and difference Fourier methods. Refinement by full-matrix least squares using *SHELX*76 (Sheldrick, 1976), anisotropic for non-H atoms, isotropic for H atoms, $w = 1/[\sigma^2(F) + 0{\cdot}00457F^2]$, $\sum w(|F_o| - |F_c|)^2$ minimized. Final R factors were $R = 0{\cdot}044$ and $wR = 0{\cdot}053$ for 2908 observed reflections. $(\Delta/\sigma)_{\max} = 0{\cdot}22$, $\Delta\rho_{\max} = 0{\cdot}23$ e Å^{-3}. The atomic scattering factors for C, H, O, N, Si, S and Cl used were those stored in *SHELX*76. The effects of the anomalous dispersion for Si, C and S (taken from the same reference) were included in the calculation of F_c.

Discussion. The final atomic parameters are given in Table 1.* The identification of the atoms and the

Table 1. *Fractional atomic coordinates with equivalent isotropic thermal parameters for the non-*H *and isotropic for* H *atoms (e.s.d.'s in parentheses)*

	x	y	z	U^*_{eq}/U(Å^2)
N(1)	0·2475 (2)	0·2041 (2)	0·8038 (3)	0·0471 (4)
C(1)	0·1254 (3)	0·1743 (2)	0·8358 (5)	0·0750 (8)
C(2)	0·3328 (2)	0·1533 (2)	0·7471 (3)	0·0428 (5)
O(2)	0·3281 (2)	0·0732 (1)	0·6946 (3)	0·0580 (4)
C(3)	0·4286 (2)	0·2337 (2)	0·7823 (3)	0·0412 (5)
C(4)	0·3279 (2)	0·2941 (2)	0·8384 (3)	0·0466 (5)
Si(4)	0·2689 (1)	0·4220 (1)	0·6797 (1)	0·0545 (1)
C(41)	0·2522 (4)	0·3991 (3)	0·4589 (4)	0·0818 (10)
C(42)	0·1138 (4)	0·4565 (3)	0·7245 (6)	0·0932 (11)
C(43)	0·3736 (4)	0·5321 (3)	0·7063 (6)	0·0904 (11)
C(5)	0·3497 (3)	0·2989 (2)	1·0268 (4)	0·0613 (6)
C(6)	0·5496 (2)	0·2374 (2)	0·7812 (3)	0·0426 (5)
S(6)	0·6266 (1)	0·3457 (1)	0·8471 (1)	0·0556 (1)
C(61)	0·7534 (2)	0·2824 (2)	1·0008 (3)	0·0492 (5)
C(62)	0·7459 (2)	0·1845 (2)	1·1080 (3)	0·0550 (6)
C(63)	0·8466 (3)	0·1388 (2)	1·2232 (3)	0·0581 (6)
C(64)	0·9545 (3)	0·1923 (2)	1·2344 (4)	0·0584 (6)
C(65)	0·9639 (3)	0·2910 (2)	1·1330 (4)	0·0599 (6)
C(66)	0·8634 (2)	0·3362 (2)	1·0145 (4)	0·0568 (6)
Cl(6)	1·0849 (1)	0·1346 (1)	1·3796 (1)	0·0814 (2)
Si(7)	0·6342 (1)	0·1440 (1)	0·6847 (1)	0·0481 (1)
C(71)	0·6366 (3)	0·0084 (2)	0·8192 (4)	0·0668 (7)
C(72)	0·5513 (3)	0·1524 (2)	0·4637 (4)	0·0631 (7)
C(73)	0·7959 (3)	0·1863 (3)	0·6707 (5)	0·0850 (10)
H(11)	0·101 (4)	0·189 (3)	0·937 (5)	0·105 (12)
H(12)	0·113 (3)	0·111 (2)	0·807 (4)	0·081 (10)
H(13)	0·071 (4)	0·222 (3)	0·768 (5)	0·098 (11)
H(411)	0·210 (4)	0·458 (3)	0·362 (5)	0·108 (12)
H(412)	0·326 (5)	0·397 (4)	0·440 (6)	0·145 (17)
H(413)	0·198 (5)	0·347 (4)	0·444 (7)	0·156 (17)
H(421)	0·060 (3)	0·408 (2)	0·694 (4)	0·081 (10)
H(422)	0·105 (4)	0·521 (4)	0·671 (6)	0·129 (16)
H(423)	0·137 (6)	0·478 (5)	0·817 (6)	0·202 (26)
H(431)	0·440 (5)	0·522 (4)	0·649 (7)	0·149 (17)
H(432)	0·403 (4)	0·525 (3)	0·820 (6)	0·124 (15)
H(433)	0·341 (4)	0·584 (3)	0·619 (6)	0·128 (15)
H(51)	0·379 (3)	0·237 (2)	1·092 (4)	0·083 (10)
H(52)	0·272 (3)	0·321 (3)	1·060 (5)	0·089 (11)
H(53)	0·410 (3)	0·354 (2)	1·040 (4)	0·076 (9)
H(62)	0·675 (3)	0·157 (2)	1·094 (4)	0·086 (10)
H(63)	0·842 (3)	0·070 (2)	1·295 (4)	0·061 (8)
H(65)	1·043 (3)	0·333 (2)	1·145 (4)	0·080 (10)
H(66)	0·874 (3)	0·407 (2)	0·937 (4)	0·068 (8)
H(711)	0·679 (4)	0·005 (3)	0·932 (6)	0·120 (14)
H(712)	0·669 (3)	−0·032 (3)	0·758 (5)	0·091 (11)
H(713)	0·558 (5)	−0·018 (3)	0·825 (6)	0·141 (17)
H(721)	0·465 (4)	0·144 (3)	0·461 (5)	0·114 (13)
H(722)	0·592 (4)	0·104 (3)	0·409 (5)	0·110 (13)
H(723)	0·557 (4)	0·223 (3)	0·404 (5)	0·102 (12)
H(731)	0·849 (3)	0·183 (3)	0·777 (5)	0·092 (11)
H(732)	0·806 (4)	0·260 (3)	0·617 (5)	0·100 (12)
H(733)	0·828 (4)	0·157 (3)	0·598 (5)	0·104 (12)

* $U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3$. Standard deviations of U_{eq} calculated according to Schomaker & Marsh (1983).

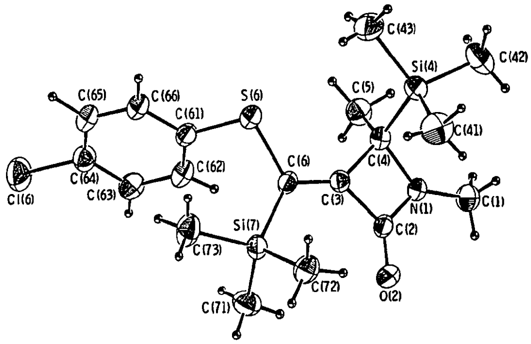


Fig. 1. *ORTEP* view of the molecule. Thermal ellipsoids scaled to enclose 40% probability. H atoms are represented as spheres of arbitrary radius.

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* Lists of structure factors, anisotropic thermal parameters and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42927 (26 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

N(1)—C(1)	1·435 (4)	C(6)—Si(7)	1·901 (3)
N(1)—C(2)	1·341 (3)	S(6)—C(61)	1·773 (3)
N(1)—C(4)	1·513 (3)	C(61)—C(62)	1·377 (3)
C(2)—O(2)	1·210 (3)	C(61)—C(66)	1·392 (4)
C(2)—C(3)	1·519 (3)	C(62)—C(63)	1·365 (4)
C(3)—C(4)	1·538 (3)	C(63)—C(64)	1·369 (4)
C(3)—C(6)	1·326 (3)	C(64)—C(65)	1·369 (4)
C(4)—Si(4)	1·898 (3)	C(64)—Cl(6)	1·748 (3)
C(4)—C(5)	1·518 (4)	C(65)—C(66)	1·374 (4)
Si(4)—C(41)	1·855 (4)	Si(7)—C(71)	1·846 (3)
Si(4)—C(42)	1·868 (5)	Si(7)—C(72)	1·850 (3)
Si(4)—C(43)	1·861 (5)	Si(7)—C(73)	1·863 (4)
C(6)—S(6)	1·781 (3)		

C(1)—N(1)—C(2)	130·3 (2)	C(3)—C(6)—S(6)	116·8 (2)
C(1)—N(1)—C(4)	133·0 (2)	C(3)—C(6)—Si(7)	122·1 (2)
C(2)—N(1)—C(4)	96·4 (2)	S(6)—C(6)—Si(7)	120·6 (1)
N(1)—C(2)—O(2)	131·4 (2)	C(6)—S(6)—C(61)	102·5 (1)
N(1)—C(2)—C(3)	91·0 (2)	S(6)—C(61)—C(62)	122·7 (2)
O(2)—C(2)—C(3)	137·6 (2)	S(6)—C(61)—C(66)	117·8 (2)
C(2)—C(3)—C(4)	88·3 (2)	C(62)—C(61)—C(66)	119·5 (2)
C(2)—C(3)—C(6)	132·9 (2)	C(61)—C(62)—C(63)	120·4 (2)
C(4)—C(3)—C(6)	138·3 (2)	C(62)—C(63)—C(64)	119·4 (3)
N(1)—C(4)—C(3)	84·1 (2)	C(63)—C(64)—C(65)	121·6 (3)
N(1)—C(4)—Si(4)	110·2 (2)	C(63)—C(64)—Cl(6)	120·1 (2)
N(1)—C(4)—C(5)	113·0 (2)	C(65)—C(64)—Cl(6)	118·3 (2)
C(3)—C(4)—Si(4)	114·6 (2)	C(64)—C(65)—C(66)	119·1 (3)
C(3)—C(4)—C(5)	115·4 (2)	C(61)—C(66)—C(65)	120·0 (3)
Si(4)—C(4)—C(5)	115·4 (2)	C(6)—Si(7)—C(71)	109·8 (1)
C(4)—Si(4)—C(41)	108·1 (1)	C(6)—Si(7)—C(72)	107·2 (1)
C(4)—Si(4)—C(42)	108·0 (2)	C(6)—Si(7)—C(73)	110·3 (1)
C(4)—Si(4)—C(43)	111·3 (2)	C(71)—Si(7)—C(72)	111·5 1)
C(41)—Si(4)—C(42)	109·3 (2)	C(71)—Si(7)—C(73)	109·6 (2)
C(41)—Si(4)—C(43)	112·0 (2)	C(72)—Si(7)—C(73)	108·4 (2)
C(42)—Si(4)—C(43)	108·1 (2)		

N(1)—C(2)—C(3)—C(4)	−2·6 (2)	C(4)—C(3)—C(6)—Si(7)	−177·3 (2)
C(2)—C(3)—C(4)—N(1)	2·4 (2)	C(4)—C(3)—C(6)—S(6)	−5·8 (5)
C(3)—C(4)—N(1)—C(2)	−2·7 (2)	C(3)—C(6)—S(6)—C(61)	130·1 (2)
C(4)—N(1)—C(2)—C(3)	2·7 (2)	Si(7)—C(6)—S(6)—C(61)	−58·2 (2)
C(2)—C(3)—C(6)—S(6)	−175·6 (2)	C(6)—S(6)—C(61)—C(62)	−30·4 (3)
C(2)—C(3)—C(6)—Si(7)	12·9 (4)	C(6)—S(6)—C(61)—C(66)	147·5 (3)

configuration of the molecule are shown in the *ORTEP* (Johnson, 1965) drawing of Fig. 1. The β-lactam ring is approximately planar with none of its four atoms deviating by more than 0·018 (3) Å from their least-squares plane. This is also shown by the small values of the torsion angles within the ring (Table 2). The bond distances in the four-membered ring are in the range observed for other 2-azetidinones. In the title compound, the bond lengths N(1)—C(2), C(2)—C(3), C(3)—C(4) and N(1)—C(4) are 1·341 (3), 1·519 (3), 1·538 (3) and 1·513 (3) Å, respectively. In our recent structural determination of 4-[(2,2-dimethylpropanoyl)oxy]-3-(1-methylethylidene)-2-azetidinone (Buynak, Rao, Pajouhesh *et al.*, 1985), the corresponding bond lengths were 1·361 (2), 1·488 (2), 1·507 (2) and 1·453 (2) Å, respectively. In 3-chloro-3-cyano-1-cyclohexyl-4-phenylthio-2-azetidinone (Chambers & Doedens, 1980), the values of these bonds are 1·348 (5), 1·561 (6), 1·566 (5) and 1·452 (5) Å, respectively.

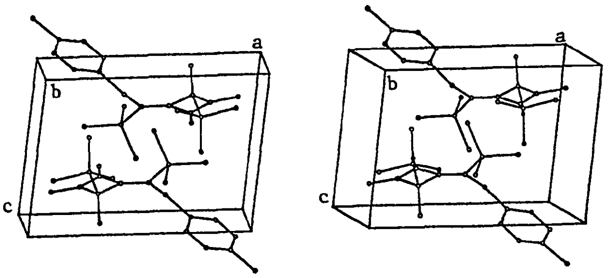

Fig. 2. Stereoscopic drawing of the molecular packing in the unit cell. H atoms excluded for clarity.

The packing of the molecules in the unit-cell is shown in Fig. 2. There is no intermolecular contact less than the van der Waals distances. The shortest intermolecular contact between non-H atoms is O(2)···C(6) [3·339 (2) Å].

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