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3-(2-Bromophenyl)-4-(triisopropylsilyl)sydnone

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Sydnones are, in most cases, extremely stable crystalline compounds that exhibit a distinct polarity. The five-membered heterocyclic ring that characterizes a sydnone is subject to electrophilic substitution. Only with a strongly activating group present will an attached aryl group compete effectively for the electrophile, due to the considerable partial positive change at the quaternary N atom of the sydnone ring. The title compound, $C_{17}H_{25}BrN_2O_2Si$, is of interest due to an intramolecular shift of the silyl-protecting group that occurs between the syndone ring and the aryl ring when treated with *n*-butyllithium. This was observed while attempting to replace the aryl bromine. With a curiosity into a rationale for this shift, we have examined a series of precursors, this being the first.

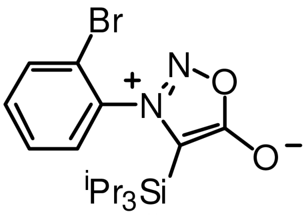
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.042
wR factor = 0.120
Data-to-parameter ratio = 26.2

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

Comment

Sydnones are dipolar heteroaromatic compounds first prepared in Sydney, Australia (Earl & Mackney, 1935). They undergo electrophilic aromatic substitution with common electrophiles and this type of reactivity has been extended to the formation of bridged ring analogs *via* intramolecular processes. For the latter, suitable *ortho*-substituted arylsydnones have been required; however, the majority of these have been available only through tedious multistep protocols from the corresponding *ortho*-substituted anilines. We have been interested in more direct routes to *ortho*-substituted arylsydnones and lithiation strategies have come to the fore. Thus, the molecule described herein was envisaged as a lithiation precursor to a variety of different *ortho*-substituted arylsydnones *via* metal-halogen exchange with *n*-butyllithium, trapping of the incipient anion with a suitable electrophile, and subsequent removal of the silyl protective group with fluoride ion. Interestingly, when an attempt was made to utilize this compound for *ortho*-substituted arylsydnone synthesis, *via* reaction with 2.2 equivalents of *n*-butyllithium at



(I)

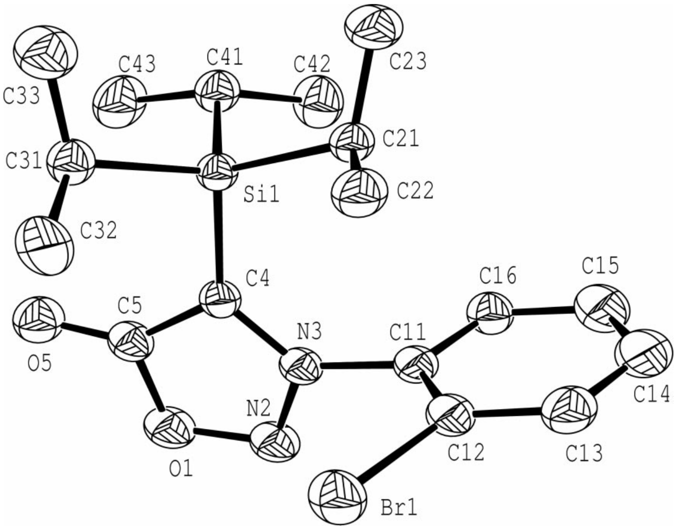


Figure 1
The molecular structure of (I) showing 30% probability displacement ellipsoids for all non-H atoms. H atoms have been omitted for clarity.

195 K in dry tetrahydrofuran, migration of the silyl moiety to the *ortho*-aryl position occurred in high yield. Accordingly, the title compound, (I), and its congeners have become valuable precursors to *ortho*-silylarylsydnones; the latter would be accessible only with difficultly by any other synthetic scheme. It is not clear from the present data how general this novel migration will be and whether or not it is an intra- or intermolecular process; however, further research will help to answer these interesting questions.

The sydnone and phenyl-ring systems found in the systems are themselves planar, but the rings within the structure lie nearly perpendicular to each other, having a dihedral angle of 80.62 (10)°. The bond distances and angles around each atom are within accepted values. In examining the molecule relative to the 1,5 shift, it is noted that the contact distance between the Si atom and Br atom is 4.81 Å, and that between Si and C12 is 4.28 Å.

Experimental

The title compound was prepared by treatment of 3-(2-bromophenyl)sydnone (Applegate & Turnbull, 1988) in dry tetrahydrofuran at 195 K with 1.5 equivalents of lithium diisopropylamide followed by 2 equivalents of triisopropylsilyl chloride.

Crystal data

$C_{17}H_{25}BrN_2O_2Si$
$M_r = 397.39$
Monoclinic, $P2_1/n$
$a = 11.7560 (18)$ Å
$b = 12.772 (2)$ Å
$c = 12.8527 (18)$ Å
$\beta = 91.820 (12)°$
$V = 1928.8 (5)$ Å^3
$Z = 4$
$D_x = 1.368$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 3.2–12.9°$
$\mu = 2.20$ mm^{-1}
$T = 296 (2)$ K
Rectangular solid with sharp bounding edges, colorless
0.35 × 0.30 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: analytical (Alcock, 1970)
$T_{\min} = 0.477$, $T_{\max} = 0.591$
6088 measured reflections
5605 independent reflections
2262 reflections with $I < 2\sigma(I)$

$R_{\rm int} = 0.012$
$\theta_{\max} = 30.0°$
$h = -16 \rightarrow 16$
$k = 0 \rightarrow 17$
$l = 0 \rightarrow 18$
3 standard reflections every 120 reflections intensity decay: <0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.120$
$S = 0.76$
5605 reflections
214 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.41$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Br1—C12	1.893 (3)	O1—C5	1.415 (4)
Si1—C31	1.883 (3)	O5—C5	1.205 (3)
Si1—C41	1.884 (3)	N3—N2	1.303 (3)
Si1—C21	1.892 (3)	N3—C4	1.360 (3)
Si1—C4	1.899 (3)	N3—C11	1.448 (3)
O1—N2	1.366 (3)		
C31—Si1—C41	109.68 (13)	O5—C5—O1	119.1 (3)
C31—Si1—C21	114.63 (13)	O5—C5—C4	135.4 (3)
C41—Si1—C21	108.53 (13)	O1—C5—C4	105.5 (2)
C31—Si1—C4	104.23 (13)	C12—C11—N3	120.6 (2)
C41—Si1—C4	107.65 (13)	C16—C11—N3	118.0 (3)
C21—Si1—C4	111.88 (12)	C11—C12—Br1	120.3 (2)
N2—O1—C5	110.5 (2)	C13—C12—Br1	119.9 (2)
N3—N2—O1	103.8 (2)	C23—C21—Si1	112.35 (19)
N2—N3—C4	117.3 (2)	C22—C21—Si1	115.16 (19)
N2—N3—C11	114.6 (2)	C32—C31—Si1	114.7 (2)
C4—N3—C11	128.0 (2)	C33—C31—Si1	112.3 (2)
N3—C4—C5	102.9 (2)	C43—C41—Si1	114.4 (2)
N3—C4—Si1	132.69 (19)	C42—C41—Si1	112.5 (2)
C5—C4—Si1	124.4 (2)		
C31—Si1—C4—N3	−137.1 (3)	C4—Si1—C41—C42	−63.4 (3)
C41—Si1—C4—N3	106.5 (3)	N2—O1—C5—O5	−178.1 (3)
C21—Si1—C4—N3	−12.7 (3)	N2—O1—C5—C4	0.8 (3)
C31—Si1—C4—C5	44.2 (3)	C5—O1—N2—N3	−0.9 (3)
C41—Si1—C4—C5	−72.2 (3)	C4—N3—N2—O1	0.6 (3)
C21—Si1—C4—C5	168.6 (2)	C11—N3—N2—O1	178.5 (2)
C31—Si1—C21—C23	−80.4 (2)	N2—N3—C4—C5	−0.1 (3)
C41—Si1—C21—C23	42.6 (2)	C11—N3—C4—C5	−177.6 (2)
C4—Si1—C21—C23	161.2 (2)	N2—N3—C4—Si1	−179.0 (2)
C31—Si1—C21—C22	45.2 (3)	C11—N3—C4—Si1	3.5 (4)
C41—Si1—C21—C22	168.2 (2)	N2—N3—C11—C12	−79.4 (3)
C4—Si1—C21—C22	−73.2 (2)	C4—N3—C11—C12	98.1 (3)
C41—Si1—C31—C32	169.7 (2)	N2—N3—C11—C16	100.9 (3)
C21—Si1—C31—C32	−67.9 (3)	C4—N3—C11—C16	−81.5 (3)
C4—Si1—C31—C32	54.7 (3)	N3—C4—C5—O5	178.2 (3)
C41—Si1—C31—C33	−63.4 (3)	Si1—C4—C5—O5	−2.7 (5)
C21—Si1—C31—C33	59.0 (3)	N3—C4—C5—O1	−0.4 (3)
C4—Si1—C31—C33	−178.4 (2)	Si1—C4—C5—O1	178.62 (18)
C31—Si1—C41—C43	−49.4 (3)	N3—C11—C12—C13	−177.2 (3)
C21—Si1—C41—C43	−175.3 (2)	C16—C11—C12—Br1	−178.1 (2)
C4—Si1—C41—C43	63.4 (3)	N3—C11—C12—Br1	2.2 (4)
C31—Si1—C41—C42	−176.2 (2)	Br1—C12—C13—C14	179.1 (2)
C21—Si1—C41—C42	57.8 (3)	N3—C11—C16—C15	178.3 (3)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD* (McArdle, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *OSCAIL* (McArdle, 1995).

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