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endo-6,*syn*-7-Dichloro-*exo*-6-phenylsulfonylbicyclo[3.1.1]heptane

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The reaction between 1-(phenylsulfonyl)tricyclo[4.1.0.0^{2,7}]heptane, (1), and nitryl chloride in $(CH_3)_2O$ gives rise to formation of a mixture of chlorination products instead of the expected nitro compounds. This mixture consists of the title compound, $C_{13}H_{14}Cl_2O_2S$, (2), and *exo*-6,*syn*-7-dichloro-*endo*-6-phenylsulfonylbicyclo[3.1.1]heptane, (3), in the ratio 88:12. The structure of the major product, (2), was established by X-ray analysis. In (2), the phenylsulfonyl group has an axial orientation, and both Cl atoms are in equatorial positions.

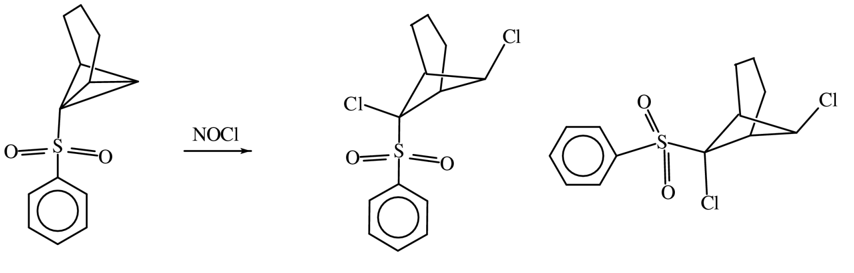
Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.004 Å
R factor = 0.033
wR factor = 0.091
Data-to-parameter ratio = 14.6

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

Comment

It is known that addition of nitryl chloride to alkenes is one of the methods for the preparation of aliphatic nitro compounds (Beger, 1967; Zyk *et al.*, 1999). Taking into account the π-like character of the central C—C bond in bicyclobutanes (Hoz, 1987), it is possible to expect addition of nitryl chloride to this bond. This could be a promising way of obtaining substituted nitrocyclobutanes. However, we have found that the reaction between nitryl chloride and one bicyclobutane derivative, (1), in $(CH_3)_2O$ leads to formation of a mixture of chlorination products (2) and (3), in the ratio 88:12, according to ^1H and ^{13}C NMR data. The formation of nitro compounds has not been observed. The major product, (2), was isolated by chromatography, crystallized and studied by X-ray diffraction (Fig. 1).



(1) (2) (3)

All bond lengths and angles in (2) are close to standard values. The C1–C6 and C2–C7 six-membered rings have sofa conformations. Atoms C1 and C7 deviate from the plane of the remaining atoms of the corresponding rings by −1.059 (3) and 1.033 (3) Å, respectively. The puckering angle for the four-membered ring is 140.9 (1)°. Both Cl atoms are in equatorial positions and the values of the relevant torsion angles, Cl1—C1—C6—C7 and Cl2—C7—C6—C1, are −147.9 (2) and 149.0 (2)°, respectively. The phenylsulfonyl group is situated in an axial position [torsion angle S1—C1—C6—C7 is 85.5 (2)°].

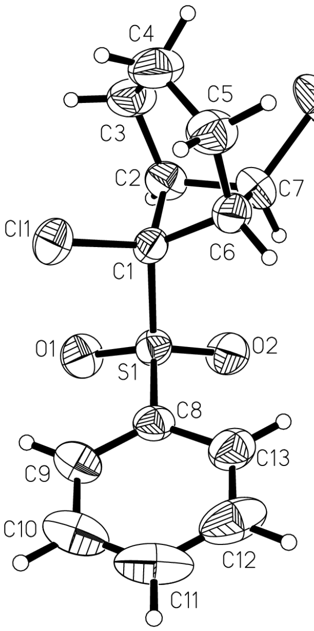


Figure 1
A view of the compound (2). The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level.

Experimental

Compounds (2) and (3) were obtained by the reaction between the previously reported compound (1) (Vasin *et al.*, 1990) and nitryl chloride. Nitryl chloride was passed, for a period of 30 min, into a solution of (1) (1.17 g) in $(CH_3)_2O$ (20 ml), containing sodium carbonate (0.5 g), with stirring and then cooled to 268 K. The reaction mixture was stirred for 1 h at 273 K. The excess nitryl chloride was removed with nitrogen until the solution became light yellow in colour. The mixture, containing (2) and (3) (88:12), was washed with 5% Na_2CO_3 solution and then with water. The organic phase was dried with calcium chloride and the solvent was evaporated in vacuum to give the mixture of products as a yellow oil (1.49 g). Compound (2) was isolated by column chromatography and crystallized from an acetone–hexane (1:3) mixture [yield 1.02 g (66.9%); m.p. 434–435 K].

Crystal data

$C_{13}H_{14}Cl_2O_2S$
$M_r = 305.20$
Monoclinic, $P2_1/n$
$a = 6.162$ (4) Å
$b = 16.710$ (11) Å
$c = 13.403$ (7) Å
$\beta = 93.58$ (4)°
$V = 1377.3$ (14) Å^3
$Z = 4$
$D_x = 1.472$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–11°
$\mu = 0.61$ mm^{-1}
$T = 173$ (2) K
Square prism, colourless
0.50 × 0.30 × 0.30 mm

Data collection

Siemens *P*3 diffractometer
$\theta/2\theta$ scans
2602 measured reflections
2372 independent reflections
1699 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.044$
$\theta_{\rm max} = 25.1°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 19$
$l = -15 \rightarrow 15$
2 standard reflections every 98 reflections intensity decay: 3.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.091$
$S = 0.99$
2372 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0625P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.31$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}

Data collection: *P*3 (Siemens, 1989); cell refinement: *P*3; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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