organic papers

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Key indicators

Single-crystal X-ray study
$T = 294$ K
Mean σ(C–C) = 0.005 Å
R factor = 0.040
wR factor = 0.102
Data-to-parameter ratio = 9.6

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

(2S,3a′R,4′R,5′S,6′R)-4′,5′-Isoprolidenedioxy-6′-(trityloxymethyl)-2′-oxotetrahydro-1H-spiro[pyrrolidine-2,3′-pyrrolo[1,2-b]isoxazole]-1-carbaldehyde

The homochiral title compound, $C_{33}H_{34}N_2O_6$, possesses normal geometrical parameters in the crystalline state.

Comment

(S)-Proline was reacted with trichloroacetaldehyde to give a single stereoisomer of oxazolidinone, (III). Treatment of compound (III) with lithium diisopropyl amide (LDA) yielded a homochiral, non-racemic enolate (Amedjkouh & Ahlberg, 2002), which can then be reacted with a variety of electrophiles, such as an alkylating reagent, to give an α-alkylated proline with retention of configuration (Seebach et al., 1983). We are interested in employing this strategy to synthesize hybrids of proline and iminosugars, which are potentially inhibitors of glycosidases. The title compound, (I), was prepared as part of this work. Its crystal structure (Fig. 1) was determined to confirm its identity and to determine the configurations of the newly formed stereocenters.
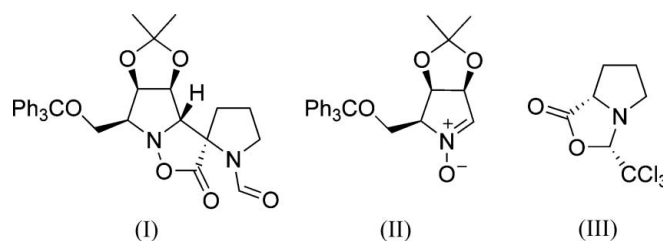
The geometrical parameters for (I) are normal. The configurations of the chiral carbon atoms are as follows: C1 R, C7 S, C8 S, C9 R, C10 S.

Experimental

The title compound, (I), was prepared from (II) and (III) following the procedure of Wang & Germanas (1999). An ice cold solution of LDA (0.25 M) in THF (10 ml) was added dropwise to a solution of 0.56 g (2.3 mmol) oxazolidinone (III) in THF (5 ml) at 195 K. After stirring for 30 min, 0.86 g (2.0 mmol) of nitrone (II) was added and the temperature was allowed to warm up to 273 K over a period of 2 h. The resulting mixture was partitioned between ethyl acetate (10 ml) and saturated NH_4Cl solution (20 ml). The aqueous layer was extracted with ethyl acetate (2 × 10 ml). The combined organic layers were dried over anhydrous Na_2SO_4. After removal of the Na_2SO_4 by filtration and evaporation of the solvents under reduced pressure, the residue was purified by silica-gel column chromatography using ethyl acetate–petrolum ether (1:1) as the eluant to afford the title compound as a white solid (0.82 g, 74%). Suitable crystals of (I) were recrystallized from ethyl acetate [m.p. 456–457 K; $[\alpha]_D^{20} = +108°$ (CHCl$_3$)]. MS (ESI): 555.2 ($C_{33}H_{34}N_2O_6$ + H, requires 555.2).

Crystal data

$C_{33}H_{34}N_2O_6$
$M_r = 554.62$
Monoclinic, $P2_1$
$a = 10.0296 (14)$ Å
$b = 12.7262 (17)$ Å
$c = 11.4028 (16)$ Å
$\beta = 98.942 (2)°$
$V = 1437.7 (3)$ Å³

$Z = 2$
$D_x = 1.281$ Mg m⁻³
Mo $K\alpha$ radiation
$\mu = 0.09$ mm⁻¹
$T = 294 (2)$ K
Block, colorless
$0.24 \times 0.20 \times 0.18$ mm

Data collection

Bruker SMART CCD
  diffractometer
ω scans
Absorption correction: multi-scan
  (*SADABS*; Bruker, 2000)
  $T_{min} = 0.979$, $T_{max} = 0.984$

8933 measured reflections
3556 independent reflections
2445 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 28.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.102$
$S = 1.08$
3556 reflections
372 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0455P)^2 + 0.0766P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.16$ e Å⁻³
$\Delta\rho_{min} = -0.17$ e Å⁻³

H atoms were positioned geometrically (C—H = 0.93–0.98 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}$(methyl C). In the absence of significant anomalous scattering effects, Friedel pairs were averaged. The absolute configuration is assigned based on the use of (3*R*,4*R*,5*S*)-nitrone, (II), as starting material.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.
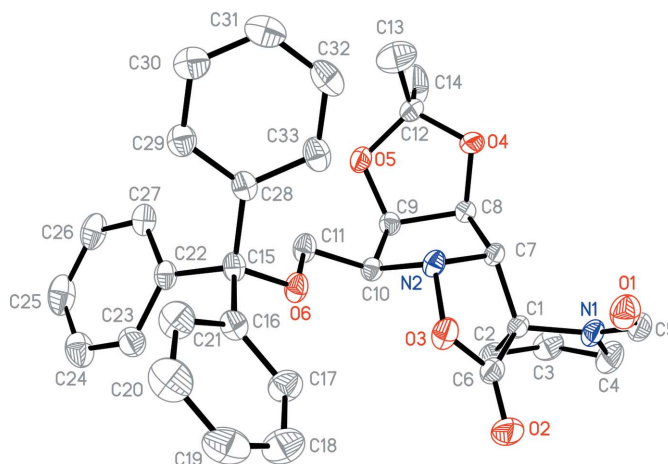

Figure 1
View of (I) showing 30% displacement ellipsoids. H atoms have been omitted for clarity.

References

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