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(4*R*)-3-Allenyl-4-(diphenylmethyl)-oxazolidin-2-one, an unsubstituted allenamide

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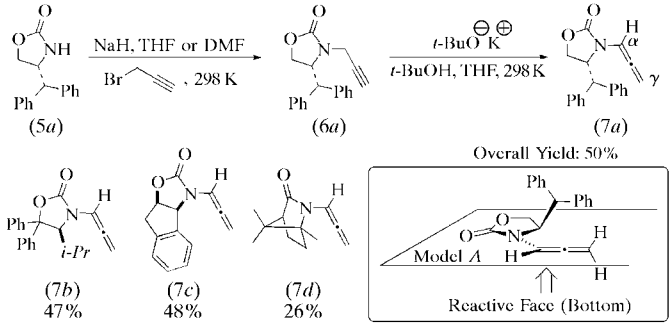
The first X-ray structure of an unsubstituted allenamide, $C_{19}H_{17}NO_2$, is reported. The solid-state phase supports the notion that a key minimum conformation of allenamides can be invoked to rationalize the observed stereochemical outcomes in many of our methodological studies employing allenamides. This minimum conformation involves two important factors, *i.e.* having approximate coplanarity between the planes of the oxazolidinone ring and the internal olefin, and having the allene moiety facing away from the carbamate carbonyl group. The C—N—C═C torsion angle that quantifies this approximate coplanarity between the plane of the oxazolidinone ring and that of the internal olefin, as determined from this crystallographic study, is −19.1 (2)°. A minimized structural calculation, which determined this angle to be −16.1°, is in close agreement. Additional structural features include a probable π–π interaction between the allene moiety and a benzene ring, and non-classical hydrogen bonding in the form of weak C—H···O interactions that are responsible for the formation of two-dimensional networks.

Comment

Allenamides have emerged as attractive building blocks in organic synthesis (Hsung *et al.*, 2003). With vastly improved stability and comparable reactivity relative to traditional allenamines, allenamides can be utilized in a diverse array of stereoselective methodologies (Achmatowicz & Hegedus, 2004; Huang *et al.*, 2002; Ranslow *et al.*, 2004; Xiong *et al.*, 2000; Wei *et al.*, 2001). In our own work, we have specifically focused on developing highly stereoselective hetero-[4+2]-cycloadditions [(1) → (2); see supplementary material; Wei *et al.*, 1999; Berry *et al.*, 2003; Rameshkumar & Hsung, 2003], oxyallyl cation [4+3]-cycloadditions [(1) → (3*a*) or (3*b*); Rameshkumar & Hsung, 2004; Xiong *et al.*, 2001, 2003] and epoxidations [(1) → (4); Rameshkumar *et al.*, 2002; Xiong *et al.*, 2002].

In all our studies, there exists a unified theme for the stereochemical outcomes. We have proposed a preferred conformation for these allenamides, in which the plane of the internal olefin is essentially coplanar with the oxazolidinone (or imidazolidinone) ring, and in which the allene moiety is facing away from the carbamate carbonyl, as shown in Model *A* of the supplementary scheme. The coplanarity ensures that the top face is blocked by the diphenyl moiety of Sibi's auxiliary [that to which the allene is attached (Sibi *et al.*, 1995)], thus favoring reactivity at the bottom face, specifically at the C2═C3 bond. The specific direction of the allene moiety then promotes the observed diastereoselectivity. If there were free rotation about the C—N bond, we would observe no diastereoselectivity in our investigations. However, we have never provided any substantial evidence to support our suggestion for a favored allenamide conformation.

Calculations were performed to determine the rotational barrier of the allene moiety in relation to the oxazolidinone ring for allenamide (7*a*) (Fig. 1). The calculations were derived from the concerted rotation of the allene around the N1—C3 bond by 360° with 180 steps (energy minimization plots can be found in the supplementary data). PM3 (Dewar *et al.*, 1985) semi-empirical calculations of the optimized geometries, using *SPARTAN* (Wavefunction, 2002), indicated that the rotational barrier is 2.89 kcal mol^{-1}. Two minima were observed, corresponding to having the allene moiety pointing away from and toward the carbamate carbonyl group, with a difference between the two of 1.70 kcal mol^{-1}. The absolute minimum conformation of the allenamide showed the allene facing away from the carbonyl group, with a C6—N1—C3═C2 torsion angle of −16.1°. Additionally, we calculated the rotational barriers and the torsion angles [corresponding to the C6—N1—C3═C2 torsion angle in (7*a*)] for chiral allenamides (7*b*)–(7*d*) and found these values to be similar to those of chiral allenamide (7*a*).



To further support our claim, we sought a single-crystal X-ray structure of an allenamide. We found only one in the Cambridge Structural Database (CSD; Version 5.25 of November 2003; Allen, 2002) (CSD refcode XOGHAC; Gaul *et al.*, 2002), which was doubly substituted at the γ position (corresponding to C1 in the present structure) of the allene. Since steric bulk on the allene influences the conformation, we were interested in the general case containing an unsubstituted allenamide. We therefore prepared the series of chiral unsubstituted allenamides (7*a*)–(7*d*), and found that allenamide (7*a*) provided X-ray quality crystals.

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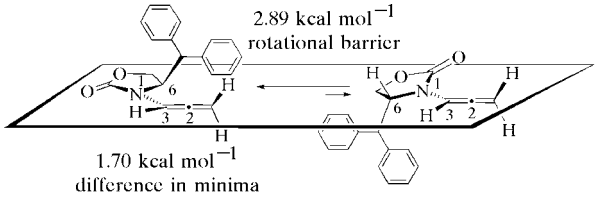

Allenamide	Rotational Barrier (kcal mol^{-1})	Minimum Energy Difference (kcal mol^{-1})	Calculated C6—N1—C3=C2 Torsion Angle (°)
(7*a*)	2.89	1.70	−16.1
(7*b*)	2.84	1.53	18.1
(7*c*)	3.05	1.69	16.1
(7*d*)	2.53	0.61	10.1

Figure 1
Minimized structures of allenamides (7*a*)–(7*d*).

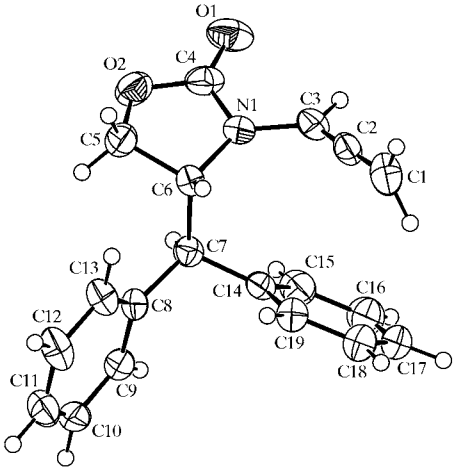

Figure 2
The structure of allenamide (7*a*). Displacement ellipsoids are drawn at the 50% probability level.

As shown in Fig. 2, the allene fragment is facing away from the carbamate carbonyl group. It is nearly coplanar with the oxazolidinone ring, as indicated by the C6—N1—C3═C2 torsion angle of −19.1 (4)°, which is in good agreement with the calculated value of −16.1°. The structural data also show the close proximity of one of the phenyl rings to the top face of the allene. The short C3···C15 distance [3.517 (4) Å] suggests the presence of a π–π interaction and further supports our notion that the diphenylmethyl moiety is within sufficient proximity to block the top face of the allene. All other bond distances and angles are unexceptional (Table 1). Intermolecular non-classical hydrogen bonding (C—H···O; Table 2) is responsible for the formation of a two-dimensional network parallel to the *ab* plane.

Experimental

For the preparation of *N*-propargylamides, NaH (60 wt% in mineral oil, 2.2 mmol) was added to a homogeneous solution of Sibi's dibenzylideneoxazolidinone (1.8 mmol) in anhydrous tetrahydrofuran (15 ml) in small portions. The resulting suspension was stirred for 30 min at room temperature before the addition of propargyl bromide (2.2 mmol). The precipitation of the sodium salt did not affect the reaction. The mixture was stirred at room temperature for 16 h, after which the mixture was concentrated and redissolved in ether (20 ml) and filtered through a small bed of celite. The solvent was concentrated under reduced pressure, and the residue was purified by flash silica-gel column chromatography (gradient solvent system 0–20% EtOAc in hexane) to provide the desired propargyl product in high yield (∼90%). For the preparation of allenamide (7*a*), KO^{t}Bu (20 mol%) was added to a homogeneous solution of the propargyl product prepared above (1.8 mmol) in anhydrous tetrahydrofuran (20 ml) under nitrogen. The reaction mixture was stirred at room temperature for 16 h and monitored by thin-layer chromatography (50% EtOAc in hexane) or ^{1}H NMR. After removing the solvent under reduced pressure, the crude mixture was redissolved in ether (20–50 ml) and filtered through a small bed of celite or basic Al_2O_3 (25% EtOAc in hexane as eluant). The solvent was removed under reduced pressure to provide pure allenamide in 50% yield over the two steps. Single crystals suitable for X-ray diffraction were grown over a period of one week at 263 K from a hexane–dichloromethane (1:1) mixture from which the dichloromethane slowly evaporated. R_F = 0.64 (50% EtOAc in hexane); m.p. 391–397 K; $[\alpha]_D^{20}$ (−) 318.3 (*c* 0.12, $CHCl_3$); $[\alpha]_D^{20}$ (−) 264.4 (*c* 1.05, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.39 (*dd*, 1H, *J* = 3.6 and 8.7 Hz), 4.49 (*dd*, 1H, *J* = 8.7 and 8.7 Hz), 4.64 (*ddd*, 1H, *J* = 3.6, 3.9 and 8.7 Hz), 4.72 (*d*, 1H, *J* = 3.9 Hz), 5.36 (*dd*, 1H, *J* = 6.6 and 10.2 Hz), 5.43 (*dd*, 1H, *J* = 6.6 and 10.2 Hz), 6.86 (*t*, 1H, *J* = 6.6 Hz), 7.07–7.38 (*m*, 10H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 49.3, 57.2, 64.9, 88.2, 96.1, 127.2, 127.7, 128.5, 128.7, 128.9, 129.2, 38.0, 139.7, 155.0, 201.4; IR (neat, cm^{-1}): 3055 (*m*), 3031 (*m*), 2924 (*m*), 1960 (*w*), 1757 (*s*), 1458 (*s*), 1266 (*s*), 889 (*m*); mass spectrum (EI): *m*/*e* (% relative intensity) 291 (53) M^+, 167 (61), 165 (39), 152 (25), 124 (100), 115 (14); *m*/*e* calculated for $C_{19}H_{17}NO_2$: 291.1259; found: 291.1260.

Crystal data

$C_{19}H_{17}NO_2$	D_x = 1.279 Mg m^{-3}
M_r = 291.34	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 1550 reflections
a = 6.2531 (10) Å	θ = 2.3–24.8°
b = 13.738 (2) Å	μ = 0.08 mm^{-1}
c = 8.8997 (14) Å	*T* = 173 (2) K
β = 98.281 (3)°	Block, colorless
V = 756.6 (2) Å^3	0.31 × 0.26 × 0.19 mm
Z = 2	

Data collection

Bruker SMART CCD area-detector diffractometer	1406 independent reflections
ω scans	1231 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scans (*SADABS*; Blessing, 1995)	R_{int} = 0.034
T_{min} = 0.975, T_{max} = 0.984	θ_{max} = 25.0°
4418 measured reflections	$h = -7 \rightarrow 7$
	$k = -16 \rightarrow 16$
	$l = -6 \rightarrow 10$

Table 1
Selected geometric parameters (Å, °).

N1—C4	1.349 (3)	C1—C2	1.291 (5)
N1—C3	1.414 (4)	C2—C3	1.292 (4)
N1—C6	1.469 (3)		
C4—N1—C3	121.0 (2)	C1—C2—C3	175.6 (3)
C4—N1—C6	111.8 (2)	C2—C3—N1	126.6 (2)
C3—N1—C6	126.8 (2)	N1—C6—C7	111.3 (2)
C6—N1—C3—C2	−19.1 (4)		

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.0499P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.034$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.079$	$\Delta\rho_{max} = 0.11$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.13$ e Å^{-3}
1406 reflections	
207 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6A···O1^{i}	1.00	2.44	3.427 (3)	168
C9—H9A···O1^{ii}	0.95	2.56	3.400 (4)	148

Symmetry codes: (i) $1 + x, y, z$; (ii) $1 - x, y - \frac{1}{2}, 1 - z$.

Because of the lack of significant anomalous scattering, Friedel equivalents were merged upon final refinement. The absolute configuration was assigned on the basis of known and unchanging chiralities of precursor molecules (see supplementary material). H atoms on the terminal end of the allene moiety (C1) were found in a difference Fourier map and refined with individual isotropic displacement parameters [C—H = 1.06 (4) and 1.04 (4) Å]. All other H atoms were placed geometrically and refined with relative isotropic displacement parameters.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1144). Services for accessing these data are described at the back of the journal.

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