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tert-Butyl 4-acetyl-2,2-dimethyl-1,3-oxazolidine-3-carboxylate

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The crystal structure of the title compound, $C_{12}H_{21}NO_4$, has been determined. The conformation in the solid state is compared to the transition state in nucleophilic addition reactions predicted by the Felkin–Anh model.

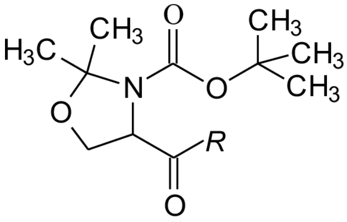
Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.104
Data-to-parameter ratio = 21.9

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

Comment

Ketone (I) has been prepared from Garner aldehyde (II) (Garner, 1984) by nucleophilic attack with methyl magnesium bromide, followed by Swern oxidation. These two homologous compounds are valuable intermediates in preparative chemistry. (I) has been initially prepared by Guanti by a different route (Guanti *et al.*, 1995). Both carbonyl compounds are used in diastereoselective alkylation reactions. The diastereoselective outcome of the reactions can be predicted by the Felkin–Anh model (Felkin *et al.*, 1968; Anh, 1980). Under non-chelating conditions, the Boc-protected N atom plays the role of the 'large' group. Nucleophilic attack on the Felkin–Anh transition state (Fig. 1) from the *si*-side is less favourable than from the *re*-side, leading to the preferred *anti* product.



(I) $R = CH_3$
(II) $R = H$

The structure of (I) with the atom numbering is shown in Fig. 2. Selected geometrical parameters are listed in Table 1. Two bifurcated intermolecular hydrogen bonds (Steiner, 2002) were found in the crystal. The strongest bond, with the major component between C23—H23*C*···O2, has an H···*A* distance of 2.54 Å, whereas the minor component, between C24—H24*A*···O2, shows an asymmetrical contact with a distance of 2.74 Å. The second bifurcated hydrogen bond is nearly symmetrical, and has a distance of 2.59 Å for the major component (C12—H12*B*···O1) and 2.66 Å for the minor component (C1—H1···O1) (Table 2).

The five-membered ring system is in a nearly perfect envelope conformation with the methylene group (C5) out of the plane (Table 1).

Compared to the conformations assumed to occur in the transition states during nucleophilic attack, (I) shows more similarity to the Cram chelate model than to the Felkin–Anh

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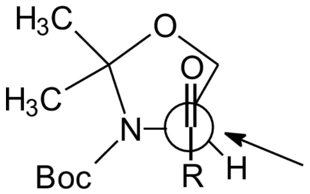

Figure 1
The structure of the Felkin–Anh transition state (R = CH$_3$, H).

model. The torsion angle N2—C1—C11—O1 is −9.76 (14)°, compared with values of −90.0° in the Felkin–Anh model and 0.0° in the Cram chelate model (Guanti *et al.*, 1995).

Experimental

Glassware was flame-dried under an argon atmosphere and allowed to cool. Anhydrous dichloromethane (50 ml) and oxalyl chloride (1.93 ml, 22.6 mmol) were added to a flask. The mixture was cooled to 195 K, and dimethyl sulfoxide was added dropwise over a period of 20 min (3.3 ml, 45.2 mmol). After warming to 213 K, *tert*-butyl 4-(1-hydroxyethyl)-2,2-dimethyl-1,3-oxazolidine-3-carboxylate (3.70 g, 15.07 mmol), dissolved in dichloromethane (15 ml), was slowly added to the mixture. After 2 h (thin-layer chromatography monitoring), the solution was warmed to 228 K and *N,N*-diisopropylamine (15.8 ml, 90.41 mmol) was added dropwise. The cooling bath was removed and ice-cold 1 *M* HCl (75 ml) added. The organic phase was separated and the aqueous phase extracted with dichloromethane. The combined organic phases were washed with phosphate buffer (pH 7), dried (Na$_2$SO$_4$) and concentrated *in vacuo*. The product was purified by flash chromatography on silica (cyclohexane–ethyl acetate, 10:1) to give colourless crystals (yield: 3.90 g, 58%) suitable for X-ray analysis.

Crystal data

C$_{12}$H$_{21}$NO$_4$
M_r = 243.30
Monoclinic, $P2_1/c$
a = 13.6452 (5) Å
b = 10.1594 (5) Å
c = 10.0848 (4) Å
β = 100.163 (2)°
V = 1376.09 (10) Å^3
Z = 4
D_x = 1.174 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 18700 reflections
θ = 1–28.3°
μ = 0.09 mm^{-1}
T = 123 (2) K
Prism, colourless
0.45 × 0.30 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
Rotation in φ and ω (2°)
Absorption correction: none
18786 measured reflections
3392 independent reflections
2879 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.032
$\theta_{\rm max}$ = 28.3°
$h = -18 \rightarrow 18$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.104
S = 1.07
3392 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0517P)^2 + 0.2788P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.32 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.26 e Å^{-3}

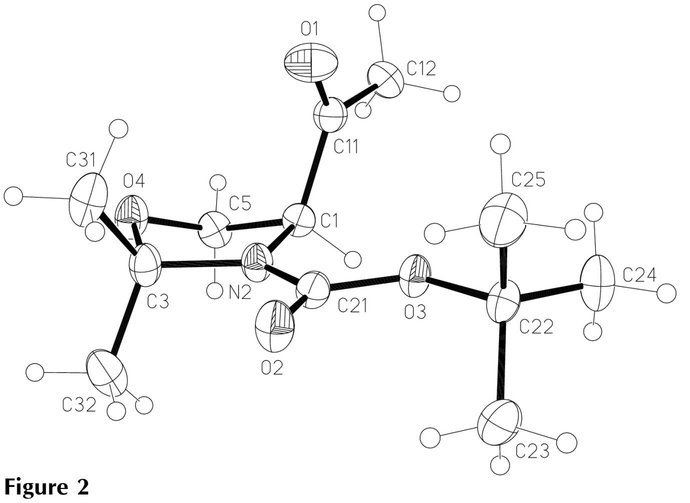

Figure 2
The structure of (I), showing the atom-numbering scheme and displacement ellipsoids at the 50% probability level for C, N and O atoms. H atoms are shown as small spheres of arbitrary radii.

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.2104 (13)	C11—C12	1.4999 (15)
O4—C5	1.4264 (13)	N2—C21	1.3578 (12)
O4—C3	1.4357 (12)	N2—C3	1.4807 (13)
C1—N2	1.4498 (12)	C3—C31	1.5167 (16)
C1—C11	1.5295 (14)	C3—C32	1.5196 (16)
C1—C5	1.5323 (13)		
C5—O4—C3	108.48 (7)	O1—C11—C1	121.68 (9)
N2—C1—C11	112.81 (8)	C12—C11—C1	115.85 (9)
N2—C1—C5	100.08 (8)	C1—N2—C3	112.00 (7)
C11—C1—C5	112.20 (8)	O4—C3—N2	102.08 (7)
O1—C11—C12	122.46 (10)	O4—C5—C1	103.61 (8)
N2—C1—C11—O1	−9.76 (14)	C1—N2—C3—O4	−3.05 (11)
C5—C1—N2—C3	−18.35 (10)	C3—O4—C5—C1	−38.01 (10)
C5—O4—C3—N2	25.74 (10)	N2—C1—C5—O4	33.05 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
C23—H23C···O2$^{\rm i}$	0.98	2.54	3.4630 (14)	156
C24—H24A···O2$^{\rm ii}$	0.98	2.74	3.7160 (15)	175
C1—H1···O1$^{\rm ii}$	1.00	2.66	3.3330 (12)	125
C12—H12B···O1$^{\rm ii}$	0.98	2.59	3.2939 (15)	129

Symmetry codes: (i) $2 - x, \frac{1}{2} + y, \frac{3}{2} - z$; (ii) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

All H atoms were treated as riding, with C—H = 0.98–1.00 Å, and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$ (CH, CH$_2$) or 1.5$U_{\rm eq}$ (CH$_3$).

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97.

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