The phenyl ring (C1*P* to C6*P*) was constrained as a regular hexagon with C—C distances of 1.390 Å. Data collection and cell refinement: *DIF*4 (Stoe & Cie, 1988*a*). Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992).

We thank the SERC for funding towards the provision of a four-circle diffractometer.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and torsion angles have been deposited with the IUCr (Reference: HA1123). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(2*RS*)-4,4-Dimethyl-2-[(1*SR*)-1-phenylethyl]-1-pyrrolidinol

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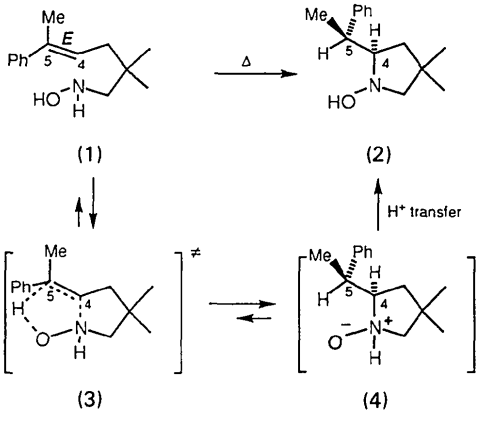
Abstract

In order to determine the stereospecificity of the thermal cyclization of [(*E*)-2,2-dimethyl-5-phenyl-4-hexenyl]hydroxylamine (1), the relative configuration of the title compound, $C_{14}H_{21}NO$, (2), has been established by single-crystal X-ray diffraction. The pyrrolidine ring adopts an envelope conformation with the N atom out of the ring plane. The molecules form hydrogen-bonded pairs through a centre of inversion [O···N 2.808 (5) Å and O—H···N 160 (4)°].

Comment

The thermal cyclization of *N*-alkenylhydroxylamines, first reported by House and co-workers (House, Manning, Melillo, Lee, Haynes & Wilkes, 1976; House & Lee, 1976) and independently discovered by us (Oppolzer, Siles, Snowden, Bakker & Petrzilka, 1979), was initially proposed to occur *via* a radical chain mechanism. As an alternative to the thermal conversion of *N*-alkenyl-*N*-methylhydroxylamines to cyclic *N*-oxides, a retro-Cope elimination mechanism has also been postulated (Ciganek, 1990). However, compelling proof of either mechanism has not yet been presented.



In order to study the alkene faciality of this process, the (*E*)-5,5-disubstituted 4-alkenylhydroxylamine (1) was cyclized by heating it in degassed benzene under reflux (18 h) to provide the *N*-hydroxypyrrolidine (2) (m.p. 358–359 K) in 81% yield. Under analogous reaction conditions, the *Z* isomer of (1) gave an epimer of (2) (oil, yield 81%) without cross contamination (Oppolzer, Spivey & Bochet, 1994).

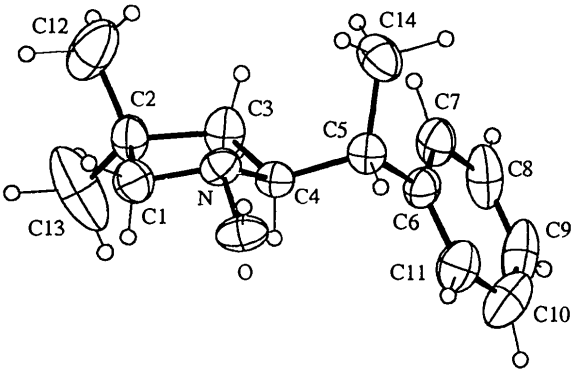


Fig. 1. View of the *N*-hydroxypyrrolidine (2) with the atomic labelling of non-H atoms shown. Ellipsoids are shown at the 30% probability level.

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The crystal structure analysis of compound (2) shows that the relative C4/C5 configuration corresponds to a suprafacial formation of the C4—N and C5—H bonds in the ring closure. This lends strong support to the retro-Cope elimination hypothesis (1→3→4→2) and militates against a radical chain mechanism for intramolecular alkene/hydroxylamine additions. This result is not only of mechanistic interest but also has relevance in organic synthesis (Oppolzer, Spivey & Bochet, 1994).

Experimental

Crystal data

$C_{14}H_{21}NO$
M_r = 219.3
Monoclinic
$P2_1/c$
a = 10.579 (2) Å
b = 11.618 (2) Å
c = 11.886 (3) Å
β = 110.293 (8)°
V = 1370.2 (5) Å^3
Z = 4
D_x = 1.063 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 30 reflections
θ = 10–12.5°
μ = 0.062 mm^{-1}
T = 298 K
Prism
0.30 × 0.25 × 0.15 mm
Colourless
Crystal source: from diethyl ether/pentane (1:1) solution

Data collection

Stoe Stadi-4 diffractometer
ω–2θ scans
Absorption correction: none
2209 measured reflections
1931 independent reflections
993 observed reflections [$F > 4.0\sigma(F)$]

R_{int} = 0.053
θ_{max} = 22.99°
$h = -11 \rightarrow 10$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 13$
2 standard reflections frequency: 45 min intensity decay: 10%

Refinement

Refinement on F
R = 0.071
wR = 0.044
S = 2.89
991 reflections
182 parameters
Only coordinates of H atoms refined for all non-methyl H atoms
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max}$ = 0.0065

$\Delta\rho_{max}$ = 0.335 e Å^{-3}
$\Delta\rho_{min}$ = −0.481 e Å^{-3}
Extinction correction: Zachariasen (1967)
Extinction coefficient: 1392 (388)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O	−0.0569 (4)	0.0864 (3)	0.5749 (3)	0.076 (2)
N	0.0070 (4)	0.1344 (3)	0.4962 (4)	0.060 (2)
C1	0.1298 (6)	0.1929 (6)	0.5679 (5)	0.080 (4)
C2	0.1563 (5)	0.2822 (5)	0.4873 (5)	0.073 (3)
C3	0.0179 (6)	0.2985 (5)	0.3905 (5)	0.076 (4)
C4	−0.0795 (5)	0.2283 (4)	0.4277 (5)	0.056 (3)
C5	−0.2057 (5)	0.1831 (4)	0.3313 (5)	0.062 (3)
C6	−0.3047 (5)	0.2805 (4)	0.2859 (5)	0.067 (4)
C7	−0.3036 (5)	0.3506 (5)	0.1937 (5)	0.076 (4)
C8	−0.3932 (8)	0.4395 (7)	0.1574 (6)	0.105 (5)
C9	−0.4842 (7)	0.4596 (7)	0.2115 (9)	0.120 (6)
C10	−0.4871 (7)	0.3941 (8)	0.3001 (9)	0.119 (7)
C11	−0.3974 (7)	0.3030 (6)	0.3392 (6)	0.089 (4)
C12	0.2532 (6)	0.2356 (7)	0.4327 (6)	0.145 (6)
C13	0.2085 (8)	0.3890 (6)	0.5515 (7)	0.179 (6)
C14	−0.1805 (5)	0.1168 (5)	0.2315 (5)	0.090 (4)

Table 2. *Selected geometric parameters* (Å, °)

O—N	1.443 (7)	C2—C13	1.461 (9)
N—C1	1.452 (7)	C3—C4	1.497 (9)
N—C4	1.473 (6)	C4—C5	1.520 (6)
C1—C2	1.504 (9)	C5—C6	1.509 (7)
C2—C3	1.527 (7)	C5—C14	1.514 (9)
C2—C12	1.49 (1)		
O—N—C1	109.0 (4)	C2—C3—C4	106.7 (5)
O—N—C4	107.7 (4)	N—C4—C3	102.0 (4)
C1—N—C4	103.7 (4)	N—C4—C5	112.1 (4)
N—C1—C2	106.0 (4)	C3—C4—C5	118.7 (5)
C1—C2—C3	103.0 (5)		
O—N—C1—C2	−155.0 (4)	C1—C2—C3—C4	5.6 (6)
C4—N—C1—C2	−40.4 (6)	C2—C3—C4—N	−29.4 (6)
O—N—C4—C3	158.2 (4)	C2—C3—C4—C5	−153.0 (5)
O—N—C4—C5	−73.8 (5)	N—C4—C5—C6	166.1 (5)
C1—N—C4—C3	42.7 (6)	N—C4—C5—C14	−65.8 (6)
C1—N—C4—C5	170.8 (5)	C3—C4—C5—C6	−75.3 (7)
N—C1—C2—C3	21.0 (6)	C3—C4—C5—C14	52.7 (6)

The H atoms of the C12 and C13 methyl substituents are disordered; two staggered positions were refined with occupancy factors of 0.5.

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *Xtal LATCON* (Hall, Flack & Stewart, 1992). Data reduction: *Xtal STARTX SORTRF*. Program(s) used to solve structure: *MULTAN*87 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1987). Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *Xtal ORTEP*. Software used to prepare material for publication: *Xtal CIFIO*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: PA1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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