

The phenyl ring (C1P to C6P) was constrained as a regular hexagon with C—C distances of 1.390 Å. Data collection and cell refinement: *DIF4* (Stoe & Cie, 1988a). Data reduction: *REDU4* (Stoe & Cie, 1988b). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1992).

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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.

References

- Blake, A. J., McNab, H. & Monahan, L. C. (1991). *J. Chem. Soc. Perkin Trans. 2*, pp. 2003–2010.
 McNab, H. & Stobie, I. (1982). *J. Chem. Soc. Perkin Trans. 1*, pp. 1845–1853.
 Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 467–473.
 Sheldrick, G. M. (1992). *SHELXTL/PC*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1993). *SHELXL93*. Univ. of Göttingen, Germany.
 Stoe & Cie (1988a). *DIF4, Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
 Stoe & Cie (1988b). *REDU4, Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

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

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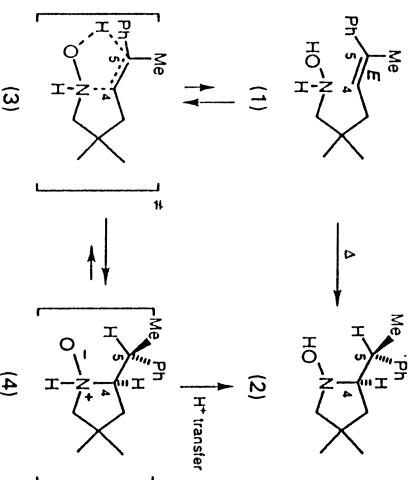
Abstract

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, C₁₄H₂₁NO, (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, Meillo, Lee, Haynes & Wilkes, 1976; House & Lee, 1976) and independently discovered by us (Oropolzer, Siles, Snowden, Bakker & Petzlikka, 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 (Oropolzer, Spivey & Bochet, 1994).

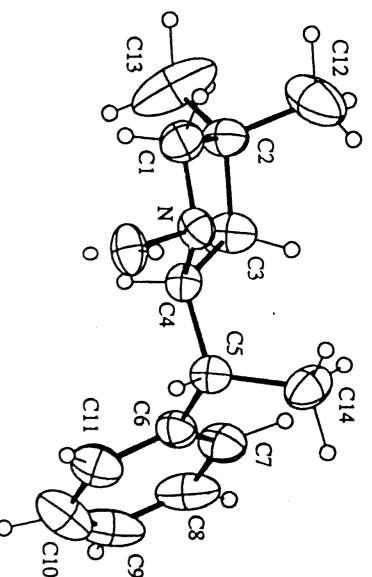


Fig. 1. View of the *N*-hydroxypyrrolidine (2) with the atomic labelling of non-H atoms shown. Ellipsoids are shown at the 30% probability level.

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

C₁₄H₂₁NO
M_r = 219.3
 Monoclinic
*P*2₁/c
a = 10.579 (2) Å
b = 11.618 (2) Å
c = 11.886 (3) Å
 β = 110.293 (8)°
V = 1370.2 (5) Å³
Z = 4
D_r = 1.063 Mg m⁻³

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

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
 $(\Delta/\sigma)_{\max} = 0.0065$

*R*_{int} = 0.053
 $\theta_{\max} = 22.99^\circ$
h = -11 → 10
k = 0 → 12
l = 0 → 13
 2 standard reflections
 frequency: 45 min
 intensity decay: 10%

$\Delta\rho_{\max} = 0.335 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.481 \text{ e \AA}^{-3}$
 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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{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—C3—C6	166.1 (5)
C1—N—C4—C3	42.7 (6)	N—C4—C3—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: DIF4 (Stoe & Cie, 1988). Cell refinement: *Xtal LATCON* (Hall, Flack & Stewart, 1992). Data reduction: *Xtal STARTX SORTRF*. Program(s) used to solve structure: *MULTAN87* (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.

References

- Giganek, E. (1990). *J. Org. Chem.* **55**, 3007–3009.
 Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal3.2 Reference Manual*. Univs. of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.
 House, H. O. & Lee, L. F. (1976). *J. Org. Chem.* **41**, 863–869.
 House, H. O., Manning, D. T., Melillo, D. G., Lee, L. F., Haynes, O. R. & Wilkes, B. E. (1976). *J. Org. Chem.* **41**, 855–863.
 Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1987). *MULTAN87. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 Oppolzer, W., Siles, S., Snowden, R. L., Bakker, B. H. & Petrzilka, M. (1979). *Tetrahedron Lett.*, pp. 4391–4394.
 Oppolzer, W., Spivey, A. C. & Bochet, C. G. (1994). *J. Am. Chem. Soc.* **116**, 3139–3140.
 Stoe & Cie (1988). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
 Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.