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5(*R*)-Isopropenyl-2-methyl-6(*R*)-[1(*R*)-methyl-2-nitroethyl]cyclohex-2-en-1-one

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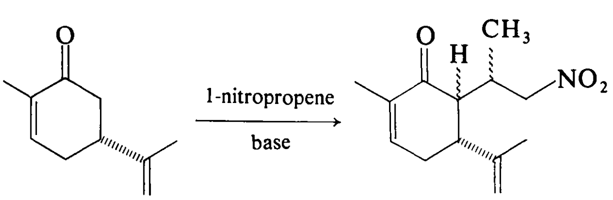
Abstract. $C_{13}H_{19}NO_3$, monoclinic, $P2_1$, $a = 8{\cdot}881$ (2), $b = 9{\cdot}408$ (2), $c = 8{\cdot}481$ (2) Å, $\beta = 111{\cdot}10$ (1)°, $Z = 2$, $D_c = 1{\cdot}19$, $D_m = 1{\cdot}18$ (1) Mg m^{-3}, $U = 661{\cdot}1$ Å^3, μ(Mo $K\alpha$) = 4·9 mm^{-1}. The final R_1 and R_2 values are 0·0421 and 0·0408 respectively, based on 1236 reflections for which $F^2 > 2\sigma(F^2)$. All 19 H atoms have been refined with isotropic Debye factors. The absolute configuration at C(11) has been shown to be *R*, based upon the known absolute configuration of (–)-carvone.

Introduction. The use of nitroethene or 1-nitropropene as bicycloannulation reagents in one-step syntheses of tricyclic species has recently been described (Cory, Anderson, McLaren & Yamamoto, 1981). During studies of the bicycloannulation of (–)-carvone with 1-nitropropene, a 75% combined yield of two diastereomeric adducts (in a ratio of 4 to 1) was obtained by quenching the reaction at 195 K with acetic acid (see scheme). In order to establish the stereochemistry of the major adduct, a single-crystal X-ray study was undertaken. Crystals suitable for analysis were obtained by recrystallization from ethanol. Weissenberg and precession photography established the space group as $P2_1$; systematic absences 0*k*0 for *k* odd. The crystal (approximate dimensions 0·42 × 0·19 × 0·14 mm) was centered and aligned on a Picker FACS-1 four-circle diffractometer, controlled by the Vanderbilt operating system (Lenhert, 1975). Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71070$ Å), monochromatized by graphite, was used to record 1798 observations out to a 2θ maximum of 50°. Six standard reflections, 020, 0$\bar{2}$0, 100, 011, 002 and 00$\bar{2}$, were monitored regularly. Only random variations were observed until, after 800 observations had been recorded, a power failure interrupted data collection. Subsequent measurements showed a 20 (2)% uniform decrease in counts; a correction was made in the later stages of refinement. Nine crystal faces were identified as forms {100}, {001} and {1$\bar{1}$1}, and faces (01$\bar{1}$), (101) and ($\bar{1}$01). No absorption correction was made. The raw data were corrected for background, monochromator polarization and Lorentz–polarization effects, and standard deviations assigned as described elsewhere (Payne, 1973). *p* was chosen as 0·03 (Busing & Levy, 1957).



After many unsuccessful attempts to solve the structure by direct methods, a solution was obtained by a Patterson search approach (Tollin, 1966), utilizing the known geometry of the C_9O fragment formed by the six-membered ring and the four atoms to which it is bonded. Refinement was by full-matrix least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weight w is defined as $4F_o^2/\sigma^2(F_o^2)$. Agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}093$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0{\cdot}099$ were obtained, with all 17 non-H atoms assigned anisotropic thermal parameters. Atomic scattering factors for neutral O, N and C atoms were taken from *International Tables for X-ray Crystallography* (1974), and those for H from Stewart, Davidson & Simpson (1965). The chosen model had the absolute configuration known to be that of (–)-carvone (Klein & Ohloff, 1963). The 19 H atoms were readily located in a difference Fourier synthesis; their inclusion with fixed isotropic Debye factors reduced R_1 to 0·054 and R_2 to 0·051. Subsequent refinement of their thermal parameters gave an acceptable geometry, and converged at $R_1 = 0{\cdot}050$ and $R_2 = 0{\cdot}046$.

At this stage a decay correction was introduced, whereby all later observations were multiplied by 1·25. A significant reduction in the magnitudes of the thermal parameters and an improvement in the agreement factors were observed. Refinement finally converged at $R_1 = 0{\cdot}0421$ and $R_2 = 0{\cdot}0408$ for 1236 observations and 229 variables. A total difference Fourier synthesis contained no peak larger than 0·22 (6) e Å^{-3}, there was no evidence for secondary extinction, and a statistical analysis of R_2 in terms of $|F_o|$, indices, $\lambda^{-1}\sin\theta$, and diffractometer setting angles χ and φ showed no

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unusual trends. The final positional parameters and their e.s.d.'s are given in Table 1.*

Discussion. The crystals are built up from discrete molecules, for only two intermolecular distances were observed less than 2·5 Å: 2·47 (5) Å, between O(1) and H2C(13) at $1-x, \frac{1}{2}+y, 1-z$, and 2·49 (6) Å, between H2C(4) and H2C(12) at $1-x, y-\frac{1}{2}, -z$. Fig. 1 shows the atom-numbering scheme, while Fig. 2 is a stereoview of the molecule. Selected intramolecular distances and angles are given in Table 2. The results from the refinement were satisfactory; C—H bond lengths varied from 0·77 (5) to 1·16 (5) Å, a mean of 0·97 (9) Å. Angles at sp^3 C atoms (including the three methyl groups) had a mean of 108 (7)°, and at sp^2 C atoms a mean of 119 (4)°.

Table 1. *Positional parameters* (×10⁴) *and thermal parameters* (Å² × 10³) *with e.s.d.'s in parentheses*

The temperature factor is given by $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. $U_{ij} = \beta_{ij}/(2\pi^2 a_i^* a_j^*)$ and $U_{eq} = \frac{1}{3}\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq} or U
O(1)	4019 (3)	2000	4178 (4)	73 (2)
O(2)	9740 (4)	−172 (5)	6531 (4)	93 (2)
O(3)	8964 (4)	1098 (5)	8140 (4)	97 (2)
N	8713 (4)	417 (5)	6864 (5)	59 (2)
C(1)	3819 (5)	1079 (5)	3121 (4)	47 (2)
C(2)	2231 (4)	447 (6)	2307 (5)	55 (2)
C(3)	2030 (6)	−561 (6)	1173 (6)	58 (3)
C(4)	3312 (5)	−1145 (6)	665 (6)	53 (2)
C(5)	4986 (4)	−956 (5)	2004 (5)	41 (2)
C(6)	5207 (4)	615 (5)	2605 (4)	38 (2)
C(7)	866 (7)	1027 (10)	2786 (9)	93 (4)
C(8)	6284 (5)	−1472 (6)	1411 (5)	50 (2)
C(9)	7156 (6)	−2594 (7)	2114 (7)	78 (3)
C(10)	6514 (7)	−741 (8)	−30 (7)	74 (3)
C(11)	6880 (4)	925 (5)	3932 (4)	42 (2)
C(12)	7370 (7)	2485 (6)	4048 (7)	61 (3)
C(13)	7021 (5)	353 (7)	5647 (5)	55 (2)
HC(3)	1204 (58)	−902 (55)	708 (60)	91 (19)
H1C(4)	3074 (41)	−2104 (48)	454 (44)	58 (12)
H2C(4)	3299 (42)	−692 (37)	−393 (51)	64 (12)
HC(5)	4909 (36)	−1511 (35)	2899 (39)	40 (9)
HC(6)	5188 (37)	1151 (38)	1636 (42)	44 (10)
H1C(7)	−86 (64)	580 (53)	2278 (59)	105 (18)
H2C(7)	1136 (58)	843 (58)	4092 (64)	113 (18)
H3C(7)	576 (77)	2006 (84)	2916 (82)	169 (29)
H1C(9)	6901 (42)	−3083 (42)	2936 (47)	53 (12)
H2C(9)	7941 (52)	−2928 (49)	1617 (50)	85 (14)
H1C(10)	5333 (82)	−663 (64)	−865 (76)	162 (28)
H2C(10)	7475 (63)	−1259 (62)	−476 (66)	132 (19)
H3C(10)	6830 (59)	246 (67)	252 (54)	101 (18)
HC(11)	7654 (33)	403 (31)	3658 (32)	27 (8)
H1C(12)	8527 (49)	2577 (41)	4867 (45)	62 (11)
H2C(12)	7271 (45)	2804 (45)	2953 (54)	71 (14)
H3C(12)	6680 (52)	2988 (52)	4353 (51)	79 (18)
H1C(13)	6185 (52)	792 (51)	6251 (48)	89 (14)
H2C(13)	6645 (44)	−478 (47)	5600 (44)	52 (12)

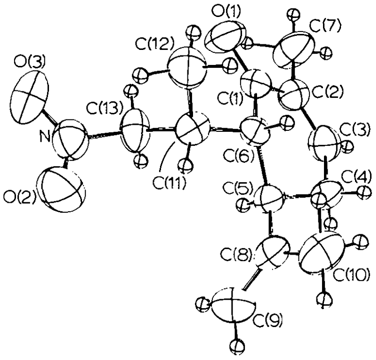

Fig. 1. The atom-numbering scheme.

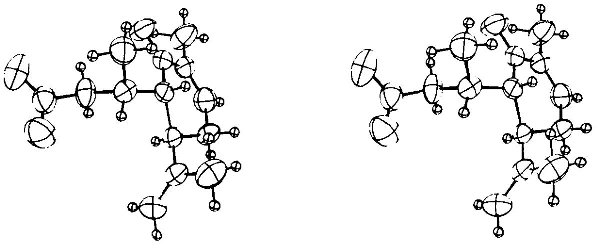

Fig. 2. A stereoview of the molecule with atoms drawn as 50% probability thermal ellipsoids.

Table 2. *Intramolecular bond distances* (Å) *and angles* (°)

C(1)—O(1)	1·213 (4)	C(6)—C(11)	1·535 (5)
C(1)—C(2)	1·455 (5)	C(8)—C(9)	1·318 (6)
C(1)—C(6)	1·513 (5)	C(8)—C(10)	1·479 (6)
C(2)—C(3)	1·316 (5)	C(11)—C(12)	1·524 (6)
C(2)—C(7)	1·512 (6)	C(11)—C(13)	1·513 (5)
C(3)—C(4)	1·462 (6)	N—C(13)	1·486 (5)
C(4)—C(5)	1·522 (5)	N—O(2)	1·185 (4)
C(5)—C(6)	1·553 (5)	N—O(3)	1·207 (4)
C(5)—C(8)	1·495 (5)		
O(1)—C(1)—C(2)	120·1 (3)	C(5)—C(6)—C(11)	113·4 (3)
O(1)—C(1)—C(6)	120·1 (3)	C(1)—C(6)—C(11)	114·1 (3)
C(2)—C(1)—C(6)	119·7 (3)	C(5)—C(8)—C(9)	120·4 (5)
C(1)—C(2)—C(7)	117·3 (4)	C(5)—C(8)—C(10)	118·7 (4)
C(1)—C(2)—C(3)	119·6 (4)	C(9)—C(8)—C(10)	120·9 (5)
C(3)—C(2)—C(7)	123·0 (5)	C(6)—C(11)—C(12)	114·2 (3)
C(2)—C(3)—C(4)	124·8 (4)	C(6)—C(11)—C(13)	111·1 (3)
C(3)—C(4)—C(5)	113·0 (4)	C(12)—C(11)—C(13)	111·0 (4)
C(4)—C(5)—C(8)	112·0 (3)	C(11)—C(13)—N	111·5 (4)
C(4)—C(5)—C(6)	109·3 (3)	C(13)—N—O(2)	119·2 (4)
C(6)—C(5)—C(8)	113·4 (3)	C(13)—N—O(3)	117·3 (4)
C(5)—C(6)—C(1)	110·5 (3)	O(2)—N—O(3)	123·5 (4)

Some weighted least-squares planes are given in Table 3. Both the nitro fragment and the isopropenyl group are planar, within experimental error, though

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* Lists of structure factors, anisotropic and isotropic thermal parameters, and bond distances and bond angles defined by H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35949 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Weighted least-squares planes*

Distances from the plane are given in Å.

Plane *A*: $3·005x + 7·733y - 4·657z = -2·515$			
N	−0·005 (4)	O(2)	0·003 (5)
C(13)	0·005 (6)	O(3)	0·003 (5)
Plane *B*: $4·110x + 5·669y + 3·732z = 2·260$			
C(5)	−0·005 (4)	C(10)	−0·015 (7)
C(8)	0·014 (4)	H1C(9)	−0·07 (3)
C(9)	−0·001 (5)	H2C(9)	−0·05 (4)
Plane *C*: $-2·940x - 6·499y + 5·817z = 1·002$			
O(1)	0·010 (2)	C(4)	0·032 (6)
C(1)	0·000 (4)	C(6)	−0·039 (4)
C(2)	−0·016 (4)	C(7)	−0·074 (9)
C(3)	−0·015 (5)	HC(3)	−0·04 (5)

some twisting is apparent [see the displacements of C(4), C(6) and C(7)] in the α,β-unsaturated ketone moiety.

Bond distances and bond angles are all in good agreement with those determined for similar diastereoisomers of cyclohexanone by Calligaris, Giordano & Randaccio (1966) and Calligaris, Manzini, Pitacco & Valentin (1975).

The absolute configuration at C(11) has been determined to be *R* based upon the known absolute configuration of (−)-carvone. Furthermore, the stereochemistry of the title compound is that required for the production of the major bicycloannulation product (Cory *et al.*, 1981).

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Pivaloyl-glycyl-*N*′-méthyl-L-prolinamide Monohydratée

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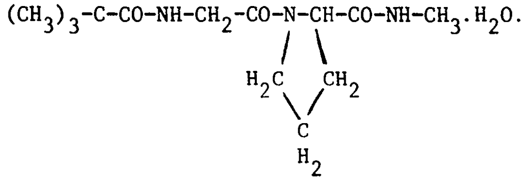
Abstract. $C_{13}H_{23}N_3O_3.H_2O$, tetragonal, space group $P4_3$, $a = 9·806\ (1)$, $c = 16·253\ (3)$ Å, $V = 1563$ Å^3, $d_x = 1·22$ Mg m^{-3}, $Z = 4$ ($T = 293$ K). The final R_F is 0·048 for 917 observed reflections. Molecular conformations show opened forms stabilized by a three-dimensional network of hydrogen bonds.

Introduction. Dans le cadre de l'étude systématique des séquences dipeptidiques contenant le résidu proline et protégées aux deux extrémités par des fonctions amides (Aubry, Protas, Boussard & Marraud, 1977, 1979, 1980*a*,*b*; Boussard, Marraud & Néel, 1974; Boussard, Marraud & Aubry, 1979), nous présentons ici la structure cristalline de la pivaloyl-glycyl-*N*′-méthyl-L-prolinamide monohydratée (*t*BuCO-Gly-L-Pro-NHMe) de formule:


$(CH_3)_3\text{-C-CO-NH-}CH_2\text{-CO-N-CH-CO-NH-}CH_3.H_2O$