

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1282). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 933–936

Two 1,5-Disubstituted Proline Esters

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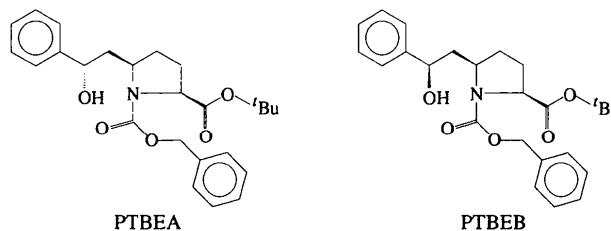
(Received 29 November 1996; accepted 24 January 1997)

Abstract

The absolute configurations of two diastereoisomers, (2*S*,5*R*)-*cis*-1-benzyloxycarbonyl-5-[(2*S*)-hydroxy-2-phenylethyl]-2-proline *tert*-butyl ester (PTBEA, C₂₅H₃₁NO₅) and (2*S*,5*R*)-*cis*-1-benzyloxycarbonyl-5-[(2*R*)-hydroxy-2-phenylethyl]-2-proline *tert*-butyl ester (PTBEB, C₂₅H₃₁NO₅), have been established by X-ray analysis. Partial disorder of the two methylene groups of the proline ring was observed in the structure of PTBEA. In both structures, the crystal packing is controlled by an O—H···O hydrogen bond between the hydroxyl and carbonyl groups of the benzyloxycarbonyl moiety.

Comment

The structural studies of PTBEA and PTBEB were undertaken in order to establish the absolute configuration adopted by the hydroxy-substituted C atom in both compounds, the absolute configurations of the two other asymmetric centres (C2 and C5) being already known. Single crystals of PTBEA and PTBEB were obtained by a new synthetic route proposed by Chiesa, Manzoni & Scolastico (1996). The procedure uses (2*S*)-pyroglutamic acid as starting material and requires, in an intermediate step, a Lewis acid-promoted allylation at position 5, yielding products with an observed *cis* selectivity, as confirmed also by the present X-ray studies of the title diastereoisomers. The target of the synthesis proposed by the cited authors was to obtain 2,5-disubstituted pyrrolidine derivatives with a hydroxyethyl or hydroxypropyl group at the 5 position, these derivatives being suitable precursors of conformationally restricted peptidomimetics (Colombo *et al.*, 1994, 1995). The latter compounds are the object of increasing interest as potential new bioactive molecules, providing valuable information on the conformation of the mimicked peptide in its complex with the receptor (Robl *et al.*, 1994; Williams *et al.*, 1993; Gleason & Johnson, 1993).



The numbering schemes adopted in the present analysis for compounds PTBEA and PTBEB are shown in Figs. 1 and 2, respectively. The structure of PTBEA was found to be affected by disorder of the C10 and C11 atoms of the proline ring. In both structures, the *cis* conformation is confirmed by the values assumed by the torsion angles C8—C9—C10—C11 [145.3(2)° for PTBEB, and 91.8(4) and 146.6(2)°, respectively, for groups A and B of PTBEA] and C10—C11—C12—C13 [−85.3(2)° for PTBEB, and −142.6(3) and −84.9(3)° for groups A and B of PTBEA]. The proline rings of the two molecules show a twisted conformation, with a torsion angle C9—C10—C11—C12 of −37.8(2)° for PTBEB and of 41.5(5) and −44.0(3)°, respectively, for groups A and B of PTBEA. The crystal packing of both structures is characterized by O5—HO5···O1 intermolecular hydrogen bonding between the hydroxyl group and the carbonyl group of the benzyloxycarbonyl moiety [molecule at (2−*x*, ½−*y*, 1−*z*) for PTBEA and at (1−*x*, ½+*y*, −*z*) for PTBEB], with O···O separations of 2.763(2) and 2.787(2) Å in PTBEA and PTBEB, respectively.

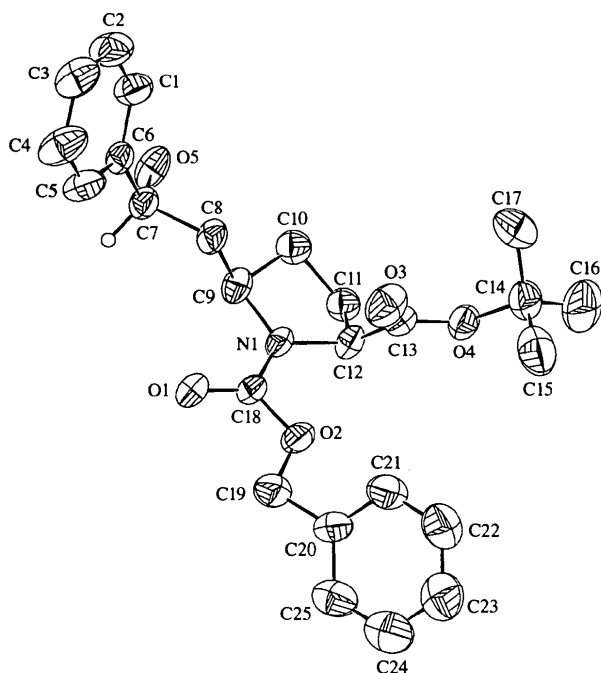


Fig. 1. View of PTBEA showing the atom-labelling scheme and 40% probability displacement ellipsoids for non-H atoms. The B conformation of the disordered proline ring is drawn. Only the H atom at C7 is shown.

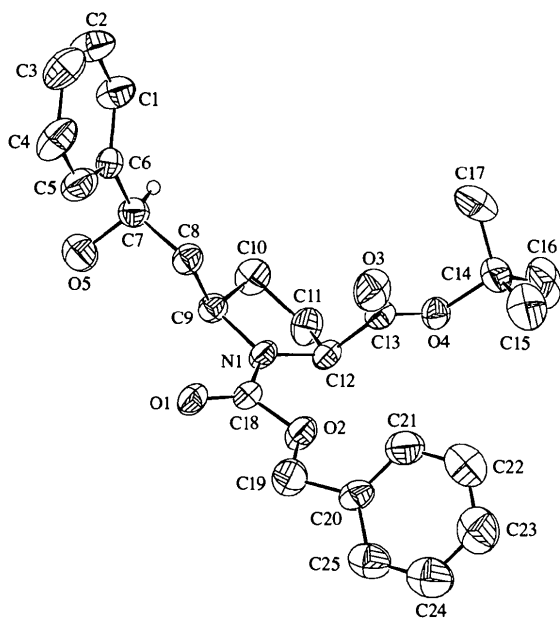


Fig. 2. View of PTBEB showing the atom-labelling scheme. Ellipsoids and H atoms are as in Fig. 1.

Experimental

Crystalline solids of PTBEA and PTBEB were obtained according to Chiesa, Manzoni & Scolastico (1996).

PTBEA

Crystal data

C₂₅H₃₁NO₅
M_r = 425.51
 Monoclinic
*P*2₁
a = 11.735 (1) Å
b = 9.683 (1) Å
c = 11.985 (1) Å
 β = 118.87 (1)°
V = 1192.6 (2) Å³
Z = 2
D_x = 1.185 Mg m⁻³
D_m not measured

Mo K α radiation
 λ = 0.71073 Å
 Cell parameters from 60 reflections
 θ = 14.94–24.98°
 μ = 0.082 mm⁻¹
T = 293 (2) K
 Prism
 0.50 × 0.44 × 0.24 mm
 Colourless

Data collection

Siemens P4 diffractometer
 2 θ / ω scans
 Absorption correction: none
 16 790 measured reflections
 4204 independent reflections
 3651 reflections with
 $I > 2\sigma(I)$
*R*_{int} = 0.0331

θ_{\max} = 25°
h = -13 → 13
k = -11 → 11
l = -14 → 14
 3 standard reflections
 every 97 reflections
 intensity decay: 4.37%

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.030
wR(*F*²) = 0.083
S = 1.018
 4204 reflections
 388 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0552P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = -0.001$
 $\Delta\rho_{\max} = 0.159 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.107 \text{ e \AA}^{-3}$

Extinction correction:
 SHELXL93 (Sheldrick,
 1993)
 Extinction coefficient:
 0.018 (3)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)
 Absolute configuration:
 Flack (1983)
 Flack parameter = 0.2 (7)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²) for PTBEA

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} / <i>U</i> _{eq}
O1	0.95222 (12)	0.43128 (14)	0.68858 (11)	0.0694 (3)
O2	0.84155 (12)	0.41595 (12)	0.79786 (10)	0.0610 (3)
O3	0.57205 (14)	0.5460 (2)	0.58886 (13)	0.0878 (4)
O4	0.54754 (10)	0.69390 (13)	0.72104 (10)	0.0617 (3)
O5	0.91116 (14)	0.84569 (13)	0.43296 (11)	0.0714 (4)
N1	0.83383 (12)	0.61069 (13)	0.69646 (11)	0.0496 (3)
C1	0.8731 (2)	0.5133 (2)	0.2692 (2)	0.0730 (5)
C2	0.8214 (3)	0.4595 (2)	0.1470 (2)	0.0918 (7)
C3	0.7420 (2)	0.5395 (2)	0.0448 (2)	0.0825 (6)
C4	0.7147 (2)	0.6711 (2)	0.0634 (2)	0.0810 (6)
C5	0.7650 (2)	0.7243 (2)	0.1856 (2)	0.0667 (5)
C6	0.84488 (14)	0.6456 (2)	0.28984 (13)	0.0501 (3)
C7	0.90004 (15)	0.6998 (2)	0.42493 (14)	0.0521 (4)
C8	0.8149 (2)	0.6577 (2)	0.48271 (14)	0.0567 (4)
C9	0.8700 (2)	0.7044 (2)	0.62139 (15)	0.0562 (4)
C10A†	0.8536 (7)	0.8441 (5)	0.6628 (6)	0.0577 (14)
C10B‡	0.7931 (4)	0.8395 (3)	0.6223 (4)	0.0593 (9)

C11A†	0.7317 (6)	0.8294 (5)	0.6755 (6)	0.063 (2)
C11B†	0.7888 (3)	0.8269 (3)	0.7472 (3)	0.0568 (9)
C12	0.7536 (2)	0.6770 (2)	0.74326 (15)	0.0535 (4)
C13	0.6145 (2)	0.6297 (2)	0.67373 (13)	0.0538 (4)
C14	0.4052 (2)	0.6745 (2)	0.6674 (2)	0.0764 (5)
C15	0.3827 (3)	0.5269 (4)	0.6941 (3)	0.1041 (8)
C16	0.3734 (3)	0.7741 (5)	0.7453 (4)	0.1256 (12)
C17	0.3354 (3)	0.7078 (5)	0.5269 (3)	0.1078 (9)
C18	0.88070 (15)	0.4823 (2)	0.72366 (13)	0.0507 (4)
C19	0.8852 (2)	0.2743 (2)	0.8291 (2)	0.0738 (5)
C20	0.8023 (2)	0.2047 (2)	0.87495 (15)	0.0616 (4)
C21	0.6696 (2)	0.2163 (2)	0.8108 (2)	0.0818 (6)
C22	0.5933 (3)	0.1478 (3)	0.8517 (3)	0.0956 (7)
C23	0.6502 (3)	0.0661 (3)	0.9570 (3)	0.0990 (7)
C24	0.7814 (3)	0.0533 (3)	1.0217 (2)	0.1012 (8)
C25	0.8574 (2)	0.1214 (2)	0.9815 (2)	0.0804 (6)

† U_{iso} , site occupancy = 0.381 (7). ‡ U_{iso} , site occupancy = 0.619 (7).

Table 2. Selected geometric parameters (\AA , $^\circ$) for PTBEA

O1—C18	1.211 (2)	N1—C18	1.335 (2)
O2—C18	1.345 (2)	N1—C12	1.457 (2)
O2—C19	1.449 (2)	N1—C9	1.477 (2)
O3—C13	1.204 (2)	C6—C7	1.518 (2)
O4—C13	1.325 (2)	C7—C8	1.520 (2)
O4—C14	1.484 (2)	C8—C9	1.532 (2)
O5—C7	1.418 (2)	C12—C13	1.501 (2)
O5—HO5	0.89 (3)		
C18—O2—C19	115.59 (13)	N1—C9—C8	112.63 (13)
C13—O4—C14	122.09 (14)	N1—C12—C13	112.53 (13)
C7—O5—HO5	105.3 (16)	O3—C13—O4	126.0 (2)
C18—N1—C12	125.66 (12)	O3—C13—C12	124.72 (14)
C18—N1—C9	121.03 (12)	O4—C13—C12	109.24 (13)
C12—N1—C9	113.13 (12)	O1—C18—N1	124.62 (14)
C5—C6—C7	122.04 (15)	O1—C18—O2	123.39 (14)
C1—C6—C7	119.88 (14)	N1—C18—O2	111.98 (12)
O5—C7—C6	113.24 (12)	O2—C19—C20	108.1 (2)
O5—C7—C8	107.20 (13)	C21—C20—C19	121.6 (2)
C6—C7—C8	110.95 (13)	C25—C20—C19	120.5 (2)
C7—C8—C9	112.92 (13)		

PTBEB

Crystal data

$\text{C}_{25}\text{H}_{31}\text{NO}_5$

$M_r = 425.51$

Monoclinic

$P2_1$

$a = 11.456 (1) \text{\AA}$

$b = 9.708 (1) \text{\AA}$

$c = 12.024 (1) \text{\AA}$

$\beta = 116.79 (1)^\circ$

$V = 1193.7 (2) \text{\AA}^3$

$Z = 2$

$D_x = 1.184 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Siemens P4 diffractometer

$2\theta/\omega$ scans

Absorption correction: none

16 749 measured reflections

4217 independent reflections

3091 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.0394$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{\AA}$

Cell parameters from 60 reflections

$\theta = 4.07\text{--}23.45^\circ$

$\mu = 0.082 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Prism

$0.35 \times 0.30 \times 0.29 \text{ mm}$

Colourless

$\theta_{\text{max}} = 25^\circ$

$h = -13 \rightarrow 13$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 14$

3 standard reflections

every 97 reflections

intensity decay: 7.20%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.068$

$S = 0.891$

4217 reflections

405 parameters

All H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.034P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.133 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.091 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0155 (14)

Scattering factors from

International Tables for Crystallography (Vol. C)

Absolute configuration:

Flack (1983)

Flack parameter = 0.0 (8)

Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for PTBEB

$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$				
	x	y	z	U_{eq}
O1	0.47290 (13)	0.56830 (14)	0.19819 (12)	0.0605 (4)
O2	0.35373 (14)	0.55510 (13)	0.30466 (12)	0.0592 (4)
O3	0.0813 (2)	0.6839 (2)	0.09523 (15)	0.0835 (5)
O4	0.04912 (12)	0.83976 (13)	0.21692 (11)	0.0535 (3)
O5	0.50578 (15)	0.8758 (2)	-0.03633 (13)	0.0751 (5)
N1	0.34365 (14)	0.7453 (2)	0.19745 (13)	0.0453 (4)
C1	0.2403 (2)	0.8551 (2)	-0.3324 (2)	0.0644 (6)
C2	0.2026 (3)	0.7956 (3)	-0.4478 (2)	0.0844 (8)
C3	0.2484 (3)	0.6702 (3)	-0.4573 (3)	0.0828 (8)
C4	0.3351 (3)	0.6039 (3)	-0.3519 (3)	0.0834 (8)
C5	0.3730 (3)	0.6640 (2)	-0.2367 (2)	0.0677 (6)
C6	0.3257 (2)	0.7904 (2)	-0.2254 (2)	0.0462 (4)
C7	0.3683 (2)	0.8565 (2)	-0.0990 (2)	0.0484 (4)
C8	0.3324 (2)	0.7690 (2)	-0.0138 (2)	0.0508 (5)
C9	0.3739 (2)	0.8351 (2)	0.1136 (2)	0.0478 (4)
C10	0.2989 (3)	0.9660 (2)	0.1104 (2)	0.0615 (6)
C11	0.2853 (3)	0.9653 (2)	0.2300 (2)	0.0626 (6)
C12	0.2625 (2)	0.8136 (2)	0.2456 (2)	0.0468 (4)
C13	0.1204 (2)	0.7695 (2)	0.1751 (2)	0.0492 (5)
C14	-0.0949 (2)	0.8254 (2)	0.1613 (2)	0.0611 (5)
C15	-0.1257 (4)	0.6835 (4)	0.1917 (4)	0.0942 (9)
C16	-0.1330 (3)	0.9321 (5)	0.2297 (5)	0.1091 (12)
C17	-0.1548 (3)	0.8519 (5)	0.0231 (3)	0.1042 (10)
C18	0.3955 (2)	0.6198 (2)	0.2296 (2)	0.0468 (4)
C19	0.4002 (3)	0.4159 (2)	0.3398 (3)	0.0746 (7)
C20	0.3096 (2)	0.3437 (2)	0.3783 (2)	0.0553 (5)
C21	0.1768 (3)	0.3534 (3)	0.3105 (2)	0.0746 (7)
C22	0.0945 (3)	0.2827 (3)	0.3458 (3)	0.0937 (8)
C23	0.1452 (4)	0.2010 (3)	0.4497 (3)	0.0961 (8)
C24	0.2761 (4)	0.1896 (3)	0.5169 (3)	0.0968 (9)
C25	0.3585 (3)	0.2609 (3)	0.4821 (2)	0.0743 (6)

Table 4. Selected geometric parameters (\AA , $^\circ$) for PTBEB

O1—C18	1.217 (2)	N1—C9	1.487 (2)
O2—C18	1.352 (2)	C6—C7	1.513 (3)
O2—C19	1.444 (3)	C7—C8	1.523 (3)
O3—C13	1.194 (2)	C8—C9	1.526 (3)
O4—C13	1.325 (2)	C9—C10	1.524 (3)
O4—C14	1.481 (2)	C10—C11	1.515 (3)
O5—C7	1.418 (2)	C11—C12	1.522 (3)
O5—HO5	0.84 (3)	C12—C13	1.519 (3)
N1—C18	1.334 (2)	C19—C20	1.488 (3)
N1—C12	1.457 (2)		
C18—O2—C19	115.84 (15)	C11—C10—C9	105.6 (2)
C13—O4—C14	122.15 (14)	C10—C11—C12	102.6 (2)
C7—O5—HO5	103.4 (18)	N1—C12—C13	111.45 (14)
C18—N1—C12	125.50 (14)	N1—C12—C11	102.45 (15)
C18—N1—C9	121.52 (14)	C13—C12—C11	113.8 (2)
C12—N1—C9	112.81 (14)	O3—C13—O4	126.3 (2)
C1—C6—C7	121.3 (2)	O3—C13—C12	124.3 (2)
C5—C6—C7	121.0 (2)	O4—C13—C12	109.43 (15)

O5—C7—C6	111.6 (2)	O1—C18—N1	125.2 (2)
O5—C7—C8	106.7 (2)	O1—C18—O2	122.9 (2)
C6—C7—C8	112.1 (2)	N1—C18—O2	111.89 (15)
C7—C8—C9	112.6 (2)	O2—C19—C20	108.4 (2)
N1—C9—C10	101.87 (14)	C21—C20—C19	121.8 (2)
N1—C9—C8	111.8 (2)	C25—C20—C19	120.2 (2)
C10—C9—C8	114.1 (2)		

The Flack (1983) absolute structure parameters (χ) calculated on the 'inverted' structures assumed values of 1.0 (8) and 0.8 (7) for PTBEB and PTBEA, respectively. This implies that the assignment of the absolute configuration cannot rely on the value of this parameter. Instead, it is based on the knowledge of the absolute configuration of the chiral C atom in the starting pyroglutamic acid. The observed disorder in the structure of PTBEA concerns the two methylene groups of the proline ring. Several models for interpreting the disorder were tested and the final description implies the splitting of the C10 and C11 atoms into two groups (C10A/C10B and C11A/C11B with the corresponding H atoms). These C atoms were treated isotropically with a refined partial occupancy constraint and the related H atoms were kept at calculated positions. For PTBEA, all H-atom parameters were refined, except for atoms H10A, H10B, H10C, H10D, H11A, H11B, H11C and H11D. These atoms were kept at calculated positions with $U_{iso} = 1.2U_{eq}$ of the atom to which the H atom is bonded.

For both compounds, data collection: XSCANS (Siemens, 1991); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structures: SHELXS86 (Sheldrick, 1985); program(s) used to refine structures: SHELXL93 (Sheldrick, 1993); molecular graphics: ORTEPII (Johnson, 1976); software used to prepare material for publication: SHELXL93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1080). Services for accessing these data are described at the back of the journal.

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(*cis*-1-Cyclohexyl-6-methylene-3,5,6,6a-tetrahydro-1*H*-cyclopenta[*c*]furan-4-yl)-methyl 3,5-Dinitrobenzoate

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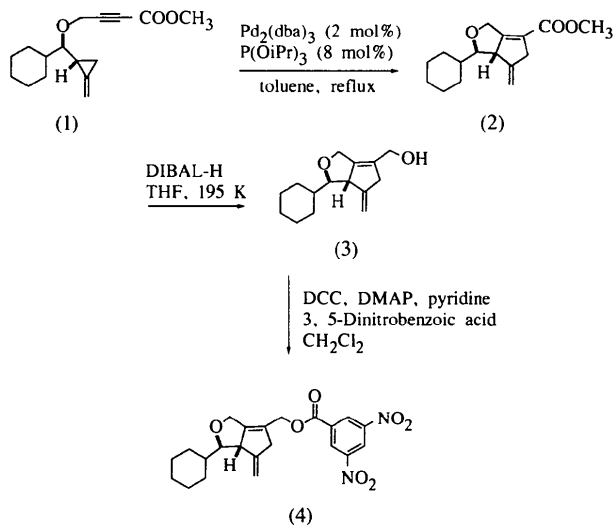
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Abstract

The structure determination of the title compound, C₂₂H₂₄N₂O₇, establishes the relative stereochemistry of the molecule.

Comment

Diastereomerically pure methylenecyclopropane, (1), undergoes intramolecular [3+2] cycloaddition in the presence of a Pd⁰ catalyst. The stereochemistry on the methylenecyclopropane ring C atom was found to be retained during the process and the reaction was shown to be stereospecific (Lautens, Ren & Delanghe, 1994). The stereochemistry of the cycloadduct could not be easily determined by NMR spectroscopy.



Pd₂(dba)₃ = Pd₂(dibenzylideneacetone)₃
 DIBAL-H = Diisobutylaluminium hydride
 DCC = Dicyclohexylcarbodiimide
 DMAP = Dimethylaminopyridine

In order to establish the stereochemistry and assign the stereochemistry in the related cycloadducts, compound (2) was converted to the corresponding 3,5-dinitrobenzoate, (4), by the following sequence: DIBAL-H