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*Acta Cryst.* (1993). **C49**, 1406–1409

### The Asymmetric Michael Process Involving Chiral Imines: Structure of (±)-*p*-Nitrobenzyl 2-(2,2-Dimethyl-1-phenylpropylamino)-1-cyclopentene-1-carboxylate

ANGÈLE CHIARONI AND CLAUDE RICHE

*Institut de Chimie des Substances Naturelles, CNRS, 91198 Gif sur Yvette CEDEX, France*

ANDRÉ GUINGANT

*Laboratoire de Synthèse Organique, Unité associée du CNRS N° 475, Faculté des Sciences et des Techniques, 2 rue de la Houssinière, 44072 Nantes CEDEX 03, France*

JEAN D'ANGELO

*Laboratoire de Chimie Organique, ERS du CNRS N° 0045, Faculté de Pharmacie, 5 rue J. B. Clément, 92296 Châtenay-Malabry, France*

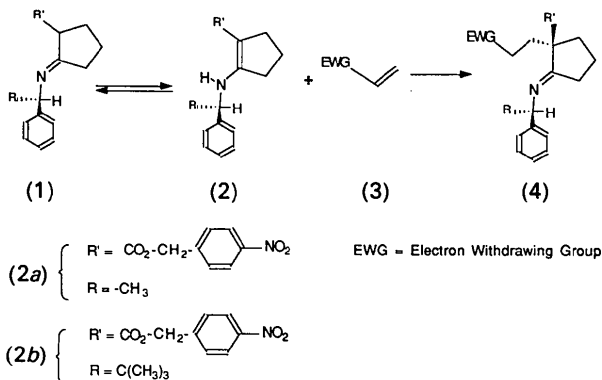
(Received 18 November 1992; accepted 8 January 1993)

## Abstract

The enantioselective synthesis of quaternary carbon centres through Michael-type alkylation of chiral imines proceeds with high enantiomeric excess with 1-phenylethylamine as auxiliary, while 2,2-dimethyl-1-phenylpropylamine was found to be completely inactive. The crystal structure of a non-reactive imine based on the latter auxiliary reveals a conformation identical with that of the reactive and highly selective 1-phenylethylamine. The phenyl ring is almost perpendicular to the enamino ester plane (torsion angle C—N—C—Ph 71.8°). The enamino ester group is planar and is stabilized by a hydrogen bond between the imine group and the carbonyl group of the ester.

## Comment

The enantioselective synthesis of quaternary carbon centres through Michael-type alkylation of chiral imines (1) was introduced in 1985 (Pfau, Reviel, Guingant & d'Angelo, 1985) and reviewed in 1992 (d'Angelo, Desmaele, Dumas & Guingant, 1992). The influence of the nature of the chiral imine on the diastereofacial differentiation has been discussed (d'Angelo, Reviel, Guingant, Riche & Chiaroni, 1989). The presence of an aromatic nucleus in the chiral auxiliary amine group appears crucial to ensure a good diastereofacial differentiation. The enantiomeric excess decreases from 90% with a phenyl group to 45% with a cyclohexyl group. Extension of this methodology to chiral enamino ester (2) ( $R' = \text{CO}_2\text{CH}_3$ ) has been reported (Guingant & Hammami, 1991) and shown to proceed with high enantiomeric excess. The X-ray structure of (2a) (d'Angelo, Reviel, Guingant, Riche & Chiaroni, 1989) revealed that the phenyl group is nearly perpendicular to the plane of the enamine. As the upper face of the enamino group is sterically



hindered by the bulky aromatic group, the attack on the opposite face should greatly predominate. Compound (2) ( $R' = \text{alkyl}$ ), where a *tert*-butyl group is substituted for the methyl group in the auxiliary amine, was found to be completely inactive (at least toward the electrophilic olefins which were used). An examination of the Dreiding models suggests that the two bulky substituents could bisect

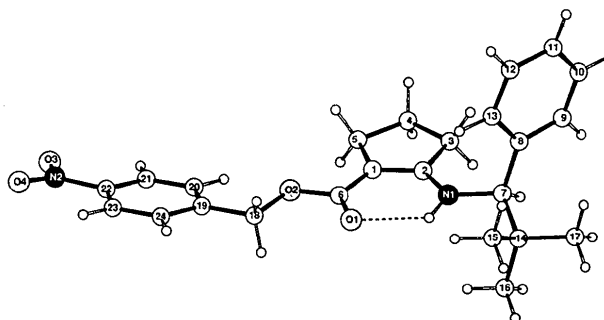


Fig. 1. General view of structure (2b) with atom-labelling scheme.

the enamino plane leading to an equal hindering of the two faces. The crystal structure of (2b) has been studied in order to determine its preferred conformation.

The X-ray analysis of (2b) (Figs. 1 and 2) shows that the phenyl ring is almost perpendicular to the enamino ester plane, as was observed in the crystal structure of (2a) (d'Angelo, Revial, Guingant, Riche & Chiaroni, 1989). A comparison of the two structures reveals that the molecules adopt an identical conformation. The crucial torsion angles C2—N1—C7—C8 and C2—N1—C7—C14 are respectively 75.5 (3) and  $-161.3$  (4) $^\circ$  in molecule (2a) ( $R$  = methyl) and 71.8 (4) and  $-161.0$  (5) $^\circ$  in molecule (2b) ( $R$  = *tert*-butyl). Moreover, the phenyl ring adopts a similar orientation with respect to the N1—C7 bond: the torsion angle N1—C7—C8—C13 is

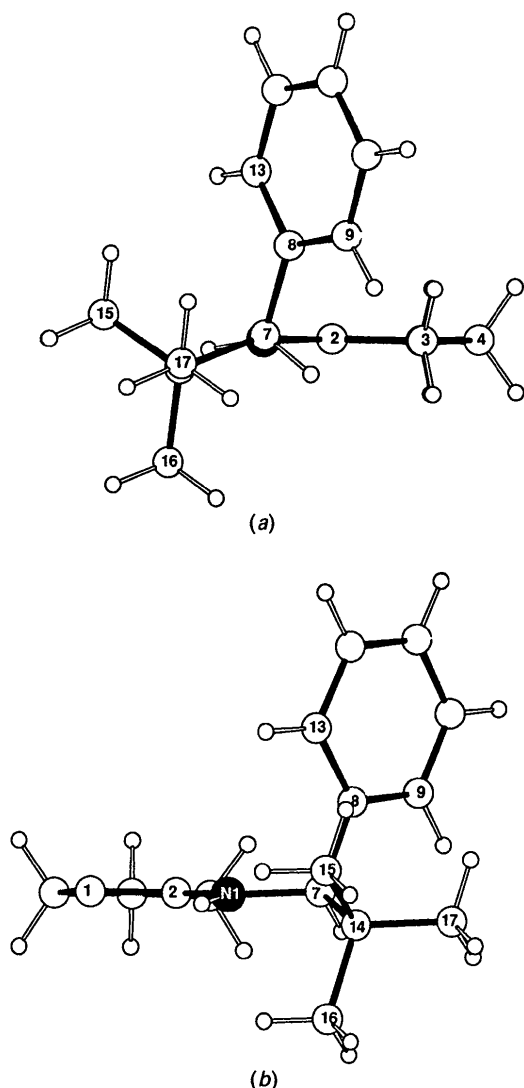


Fig. 2. Views (a) along N1—C7 and (b) perpendicular to N1—C7 showing the hindering of the C1=C2 double bond. (The *p*-nitrobenzyloxycarbonyl group is omitted for clarity.)

respectively 44.7 (3) $^\circ$  in molecule (2a) ( $R$  = methyl) and 42.8 (4) $^\circ$  in molecule (2b) ( $R$  = *tert*-butyl). The intramolecular hydrogen bond N1—H $\cdots$ O1 stabilizes the planar conformation of the enamino ester. Both the enamine and the *p*-nitrobenzyloxycarbonyl moieties are approximately planar with a maximum deviation of 0.4 Å. The cyclopentene ring, the N atom N1 and the ester group, C6, O1, O2, C18, C19, are perfectly coplanar (within 0.02 Å). This plane makes a dihedral angle of 14 $^\circ$  with the phenyl group of the *p*-nitrobenzyloxycarbonyl moiety. Only normal van der Waals contacts are observed in the crystal structures of (2a) and (2b). The cyclic enamine and the *p*-nitrobenzyloxycarbonyl moieties are stacked together at a mean distance of 4.0 Å. A view perpendicular to the enamine plane is shown in Fig. 3. Very similar stacking is observed in molecule (2a) which crystallizes in space group  $P2_1$ , while (2b) has space group  $P2_1/c$ .

As shown in Fig. 2, the  $\alpha$  face of the molecule is not hindered drastically by the *tert*-butyl group as postulated. The question of the non-reactivity of (2b) remains unanswered. Calculations are in progress in which a methyl acrylate is approached to molecules (2a) and (2b) according to the 'transition-state complex' proposed by Sevin, Tortajada & Pfau (1986).

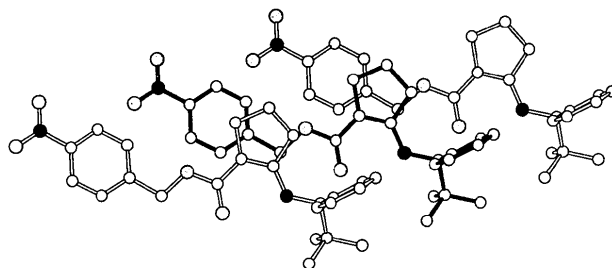


Fig. 3. Stacking of the molecules viewed perpendicularly to the enamino ester plane.

## Experimental

### Crystal data

$C_{24}H_{28}N_2O_4$   
 $M_r = 408.50$   
 Monoclinic  
 $P2_1/c$   
 $a = 6.363$  (1) Å  
 $b = 13.536$  (2) Å  
 $c = 25.703$  (4) Å  
 $\beta = 91.74$  (3) $^\circ$   
 $V = 2212.8$  (5) Å $^3$   
 $Z = 4$   
 $D_x = 1.23$  Mg m $^{-3}$

Cu  $K\alpha$  radiation  
 $\lambda = 1.5418$  Å  
 Cell parameters from 25 reflections  
 $\theta = 8.50$ –21.30 $^\circ$   
 $\mu = 0.64$  mm $^{-1}$   
 $T = 293$  K  
 Prism  
 $0.50 \times 0.30 \times 0.10$  mm  
 Yellow  
 Crystal source: from chemical synthesis

### Data collection

Nonius CAD-4 diffractometer

$R_{int} = 0.021$   
 $\theta_{max} = 64.93^\circ$

$\theta/2\theta$  scans  $h = -7 \rightarrow 7$   
 Absorption correction:  $k = 0 \rightarrow 15$   
 none  $l = 0 \rightarrow 30$   
 3853 measured reflections 1 standard reflection  
 3764 independent reflections frequency: 180 min  
 2272 observed reflections intensity variation: none  
 $[I > 3.0\sigma(I)]$

## Refinement

Refinement on  $F$  Calculated weights  
 Final  $R = 0.072$   $w = 1/[\sigma^2(F) + 0.0045F^2]$   
 $wR = 0.113$   $(\Delta/\sigma)_{\max} = 0.05$   
 $S = 1.44$   $\Delta\rho_{\max} = 0.23 \text{ e } \text{\AA}^{-3}$   
 2239 reflections  $\Delta\rho_{\min} = -0.25 \text{ e } \text{\AA}^{-3}$   
 271 parameters Atomic scattering factors  
 H-atom parameters not from *International Tables*  
 refined;  $U_{\text{iso}}(\text{H}) =$  for *X-ray Crystallography* (1974, Vol. IV, Table  
 $1.10U_{\text{eq}}(\text{bonded atom})$  2.2B)

Data collection: CAD-4 software (Enraf-Nonius, 1987). Data reduction: *NONIUS* (Riche, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1986). Program(s) used to refine structure: *SHELX76* (Sheldrick, 1976). Molecular graphics: *R3M* (Riche, 1983); *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *ACTACIF* (Riche, 1992).

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$U_{\text{eq}}$
C1	0.4983 (7)	0.5317 (3)	0.1043 (2)	0.047 (4)
C2	0.6439 (7)	0.5962 (3)	0.0870 (2)	0.044 (4)
C3	0.7964 (8)	0.5446 (3)	0.0520 (2)	0.056 (5)
C4	0.7206 (9)	0.4385 (4)	0.0494 (2)	0.073 (6)
C5	0.5305 (8)	0.4288 (3)	0.0838 (2)	0.055 (5)
C6	0.3404 (7)	0.5627 (3)	0.1386 (2)	0.049 (4)
C7	0.8119 (6)	0.7614 (3)	0.0780 (2)	0.046 (4)
C8	0.7574 (7)	0.7867 (3)	0.0213 (2)	0.045 (4)
C9	0.9129 (8)	0.7904 (4)	-0.0150 (2)	0.058 (5)
C10	0.8673 (11)	0.8168 (4)	-0.0653 (2)	0.080 (7)
C11	0.6671 (13)	0.8386 (4)	-0.0818 (2)	0.083 (8)
C12	0.5110 (11)	0.8329 (5)	-0.0469 (3)	0.089 (8)
C13	0.5519 (8)	0.8055 (4)	0.0047 (2)	0.064 (6)
C14	0.8341 (8)	0.8525 (4)	0.1138 (2)	0.055 (5)
C15	0.6253 (10)	0.9075 (4)	0.1191 (3)	0.078 (7)
C16	0.9126 (10)	0.8186 (4)	0.1673 (2)	0.078 (7)
C17	0.9910 (11)	0.9244 (5)	0.0917 (3)	0.093 (8)
C18	0.0468 (7)	0.5131 (3)	0.1871 (2)	0.057 (5)
C19	-0.0797 (7)	0.4211 (3)	0.1978 (2)	0.045 (4)
C20	-0.0101 (7)	0.3281 (3)	0.1852 (2)	0.052 (5)
C21	-0.1295 (7)	0.2462 (3)	0.1956 (2)	0.056 (5)
C22	-0.3219 (6)	0.2594 (3)	0.2174 (2)	0.045 (4)
C23	-0.3983 (7)	0.3527 (3)	0.2303 (2)	0.052 (5)
C24	-0.2729 (7)	0.4325 (3)	0.2206 (2)	0.050 (5)
N1	0.6621 (6)	0.6927 (3)	0.0990 (2)	0.050 (4)
N2	-0.4564 (7)	0.1731 (3)	0.2252 (2)	0.056 (4)
O1	0.3169 (6)	0.6459 (2)	0.1557 (2)	0.069 (4)
O2	0.2102 (5)	0.4881 (2)	0.1520 (1)	0.056 (3)
O3	-0.3846 (6)	0.0914 (3)	0.2154 (2)	0.075 (4)
O4	-0.6369 (6)	0.1855 (3)	0.2404 (2)	0.088 (5)

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

C1—C2	1.358 (6)	C11—C12	1.360 (10)
C1—C5	1.506 (6)	C12—C13	1.393 (9)
C1—C6	1.421 (6)	C14—C15	1.532 (8)
C2—C3	1.514 (6)	C14—C16	1.519 (8)
C2—N1	1.346 (6)	C14—C17	1.518 (8)

C3—C4	1.516 (7)	C18—C19	1.513 (6)
C4—C5	1.525 (8)	C18—O2	1.438 (6)
C6—O1	1.219 (6)	C19—C20	1.376 (6)
C6—O2	1.357 (5)	C19—C24	1.387 (6)
C7—C8	1.526 (6)	C20—C21	1.375 (6)
C7—C14	1.543 (6)	C21—C22	1.374 (6)
C7—N1	1.448 (5)	C22—C23	1.397 (6)
C8—C9	1.382 (7)	C22—N2	1.465 (6)
C8—C13	1.387 (7)	C23—C24	1.370 (6)
C9—C10	1.364 (8)	N2—O3	1.227 (5)
C10—C11	1.362 (11)	N2—O4	1.236 (6)
C2—C1—C5	112.3 (4)	C7—C14—C15	112.2 (4)
C2—C1—C6	121.0 (4)	C7—C14—C16	108.7 (4)
C5—C1—C6	126.7 (4)	C7—C14—C17	109.7 (4)
C1—C2—C3	110.7 (4)	C15—C14—C16	109.2 (4)
C1—C2—N1	127.1 (4)	C15—C14—C17	107.7 (5)
C3—C2—N1	122.2 (4)	C16—C14—C17	109.3 (5)
C2—C3—C4	104.8 (4)	C19—C18—O2	108.6 (4)
C3—C4—C5	108.2 (4)	C18—C19—C20	122.3 (4)
C1—C5—C4	104.0 (4)	C18—C19—C24	117.9 (4)
C1—C6—O1	126.4 (4)	C20—C19—C24	119.8 (4)
C1—C6—O2	112.7 (4)	C19—C20—C21	120.6 (4)
O1—C6—O2	120.9 (4)	C20—C21—C22	118.6 (4)
C8—C7—C14	113.9 (4)	C21—C22—C23	122.4 (4)
C8—C7—N1	111.6 (3)	C21—C22—N2	118.9 (4)
C14—C7—N1	109.8 (3)	C23—C22—N2	118.6 (4)
C7—C8—C9	120.4 (4)	C22—C23—C24	117.4 (4)
C7—C8—C13	121.3 (4)	C19—C24—C23	122.2 (4)
C9—C8—C13	118.2 (4)	C2—N1—C7	126.1 (4)
C8—C9—C10	120.9 (5)	C22—N2—O3	117.9 (4)
C9—C10—C11	121.4 (6)	C22—N2—O4	119.2 (4)
C10—C11—C12	118.6 (6)	O3—N2—O4	122.9 (4)
C11—C12—C13	121.6 (6)	C6—O2—C18	116.2 (3)
C8—C13—C12	119.3 (5)		
C2—N1—C7—C8	71.8 (4)	C4—C5—C1—C2	-0.9 (4)
C2—N1—C7—C14	-161.0 (5)	C5—C1—C2—C3	-0.2 (3)
N1—C7—C8—C13	42.8 (4)	N1—C2—C1—C6	0.7 (4)
N1—C7—C14—C16	60.5 (4)	C2—C1—C6—O1	0.1 (4)
N1—C7—C14—C15	-60.3 (4)	C2—C1—C6—O2	-179.6 (5)
N1—C7—C14—C17	-180.0 (5)	C1—C6—O2—C18	179.4 (5)
C1—C2—N1—C7	-176.6 (5)	C6—O2—C18—C19	-179.4 (5)
C1—C2—C3—C4	1.1 (4)	O2—C18—C19—C20	14.2 (3)
C2—C3—C4—C5	-1.6 (4)	C21—C22—N2—O3	5.4 (4)
C3—C4—C5—C1	1.5 (4)		

Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71048 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1038]

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*Acta Cryst.* (1993). **C49**, 1409–1410

## Structure of 1,3-Bis(triphenylphosphonium)acetone Bis(trifluoromethanesulfonate)

ANDREAS BRAM AND HANS BURZLAFF

*Institut für Angewandte Physik, Lehrstuhl für Kristallographie, Universität Erlangen-Nürnberg, Bismarckstrasse 10, D-W-8520 Erlangen, Germany*

DARIUSCH HADAWI AND HANS-JUERGEN BESTMANN

*Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42, D-W-8520 Erlangen, Germany*

(Received 16 December 1992; accepted 12 February 1993)

### Abstract

In 2-oxo-1,3-propandiylbis(triphenylphosphonium) bis(trifluoromethanesulfonate) the cation consists of two phosphane moieties which are connected by an acetone chain —CH<sub>2</sub>—CO—CH<sub>2</sub>— with the point-group symmetry 2. The central CO group lies on the twofold axis. The structure is stabilized by two SO<sub>3</sub>CF<sub>3</sub> anions.

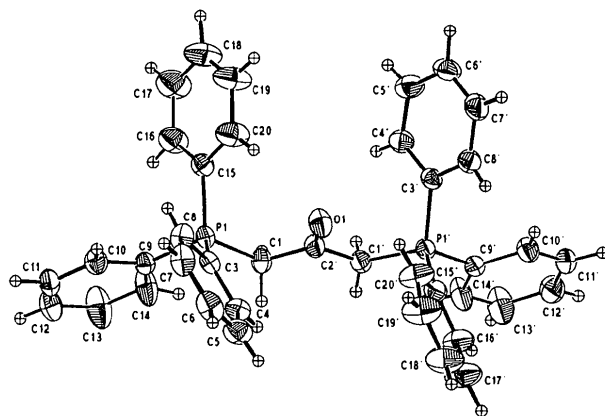
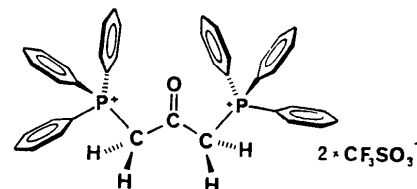


Fig. 1. View of the cation showing the atomic numbering system. The displacement ellipsoids are plotted at the 35% probability level.

### Comment

The title compound can be used to prepare arylmethylene- and alkylidene-acetylmethylenetriphenylphosphoranes (Bestmann & Schlosser, 1979), which are utilized in many ylid reactions (Cooke & Goswami, 1977; Bestmann, 1965).



### Experimental

#### Crystal data

C<sub>39</sub>H<sub>34</sub>OP<sub>2</sub><sup>2+</sup>·2CF<sub>3</sub>O<sub>3</sub>S<sup>-</sup>

*M<sub>r</sub>* = 878.79

Monoclinic

*A2/a*

*a* = 20.529 (2) Å

*b* = 17.075 (2) Å

*c* = 11.820 (1) Å

$\beta$  = 98.65 (1)°

*V* = 4096 (1) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.425 Mg m<sup>-3</sup>

Mo K $\alpha_1$  radiation

$\lambda$  = 0.70930 Å

Cell parameters from 40 reflections

$\theta$  = 7.2–16.4°

$\mu$  = 0.274 mm<sup>-1</sup>

*T* = 298 K

Brick shape

0.42 × 0.17 × 0.16 mm

Colourless

#### Data collection

Rebuilt Philips PW1100 diffractometer (Gomm, 1991)

$\theta/2\theta$  scans

Absorption correction:

none

7082 measured reflections

3416 independent reflections

2717 observed reflections

[*F* > 2.0 $\sigma$ (*F*)]

*R<sub>int</sub>* = 0.038

$\theta_{\max}$  = 24.5°

*h* = -24 → 24

*k* = 0 → 19

*l* = -13 → 13

4 standard reflections

monitored every 100

reflections

intensity variation: 1.8%

#### Refinement

Refinement on *F*

Final *R* = 0.061

*wR* = 0.059

*S* = 1.49

2717 reflections

315 parameters

All H-atom parameters re-

efined with common *U<sub>iso</sub>*

*w* = 1/[ $\sigma$ (*F<sub>o</sub>*)]

( $\Delta/\sigma$ )<sub>max</sub> = 0.01

$\Delta\rho_{\max}$  = 0.42 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.42 e Å<sup>-3</sup>

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: local software (Gomm, 1991). Cell refinement: local software (Gomm, 1991). Data reduction: local software. Program(s) used to solve structure: *SIR88* (Burla, Camalli, Cascerano, Giacovazzo, Polidori, Spagna & Viterbo, 1989). Program(s) used to refine structure: *CRYSTALS* (Watkin, Carruthers & Betteridge, 1985). Software used to prepare material for publication: *CRYSTAN* (Burzlauff & Rothammel, 1988).