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1,1,1-Trifluoro-3-phenyl-2-butyl *p*-Nitrobenzoate

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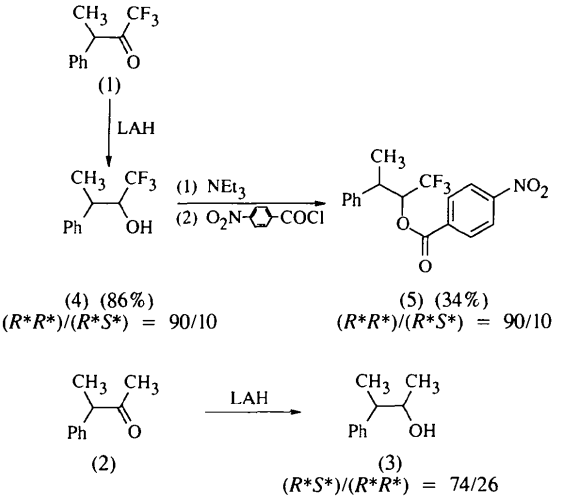
Abstract

The reduction of the trifluoromethylated ketone, 1,1,1-trifluoro-3-phenyl-2-butanone, (1), or its hydrogenated homologue, 3-phenyl-2-butanone, (2), with lithium aluminium hydride (LAH) gave 1,1,1-trifluoro-3-phenyl-2-butanol, (4), or 3-phenyl-2-butanol, (3), respectively, as a mixture of the (*R*R**)/(*R*S**) isomers. The title compound, $C_{17}H_{14}F_3NO_4$, (5), was obtained by a benzoylation reaction of the major diastereoisomer of (4). The *threo*-(*R*R**) configuration is clearly evidenced in the crystal structure of (5). So, in the reduction of (1) or (2), the *threo* isomer is the major product. It is noteworthy that the presence of the CF_3 group enhances the diastereoselectivity of the reduction reaction.

Comment

The introduction of one or more F atoms in organic compounds results in changes in their chemical reactivity. Many research groups have explored the reactivity of trifluoromethylated ketones (Begue & Bonnet-Delpon, 1991; McClinton & McClinton, 1992). It has been recognized that the CF_3 group behaves as though it is bulkier than an isopropyl group (Bott, Field & Sternhell, 1980). Bearing in mind the steric size of the CF_3 group and its electronic influence, we believe that the diastereoselectivity of the reduction reaction would be altered by the introduction of a trifluoromethyl group.

During the course of our studies (Félix, Laurent & Mison, 1995), we were interested in the diastereoselectivity of the reduction of ketone (1) with LAH. It is known that the reduction of ketone (2) with LAH leads preferentially to the formation of the *threo*-(*R*R**) isomer of alcohol (3) (Cram & Abdelhafez, 1952). The same conditions (large excess of LAH) were used to reduce ketones (1) and (2) (Félix *et al.*, 1995), and we observed a greater diastereoselectivity in the case of the formation of alcohol (4) with respect to alcohol (3) [(*R*S**)/(*R*R**) 74/26].



Analysis of the ^1H, ^{13}C and ^{19}F NMR spectra allowed us to determine the ratio of the two isomers of the benzoylated derivative (5) of alcohol (4), but did not allowed determination of the (*R*R**)/(*R*S**) configuration of the major isomer of (5). We therefore undertook the single-crystal X-ray structure analysis of this isomer. An *ORTEP* (Johnson, 1965) plot of (5) with the numbering system is shown in Fig. 1. It is clear that the major isomer of (5) has a *threo*-(*R*R**) configuration. This is in agreement with the literature (Ramachandran, Teodorovic & Brown, 1993).

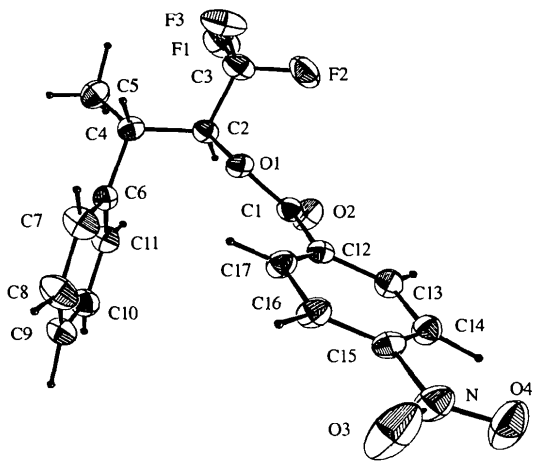


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound showing the atomic numbering scheme and 25% probability ellipsoids.

Experimental

The reduction of the trifluoromethyl ketone (1) with LAH yielded two isomers of alcohol (4). The derivative (5) was obtained by a benzoylation reaction. Colourless crystals of the major isomer of (5) were obtained from petroleum ether.

Crystal data

$C_{17}H_{14}F_3NO_4$
M_r = 353.30
Monoclinic
$P2_1/c$
a = 16.803 (4) Å
b = 7.502 (2) Å
c = 14.647 (5) Å
β = 115.39 (3)°
V = 1667.8 (9) Å^3
Z = 4
D_x = 1.407 Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 22–33°
μ = 1.06 mm^{-1}
T = 293 K
Flat
0.50 × 0.45 × 0.05 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–θ scans
Absorption correction: empirical *via* ψ scans (North, Phillips & Mathews, 1968)
T_{min} = 0.778, T_{max} = 0.948
6643 measured reflections
3324 independent reflections

2926 reflections with $I_{net}>0$
R_{int} = 0.023
θ_{max} = 73°
h = −20 → 20
k = −9 → 9
l = 0 → 18
3 standard reflections
frequency: 60 min
intensity decay: 0.8%

Refinement

Refinement on F
R = 0.057
wR = 0.067
S = 1.46
2926 reflections
268 parameters

$w = 4F_o^2/[\sigma^2(F_o^2) + 0.0036F_o^4]$
$(\Delta/\sigma)_{max}$ = 0.03
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Extinction correction: none
Only coordinates of H atoms refined
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

F1—C3	1.317 (2)	C4—C6	1.512 (2)
F2—C3	1.327 (3)	C6—C7	1.391 (2)
F3—C3	1.317 (3)	C6—C11	1.375 (2)
O1—C1	1.354 (2)	C7—C8	1.375 (3)
O1—C2	1.440 (1)	C8—C9	1.366 (4)
O2—C1	1.203 (2)	C9—C10	1.373 (3)
O3—N	1.201 (2)	C10—C11	1.379 (2)
O4—N	1.199 (2)	C12—C13	1.387 (2)
N—C15	1.477 (2)	C12—C17	1.389 (2)
C1—C12	1.486 (2)	C13—C14	1.381 (2)
C2—C3	1.509 (2)	C14—C15	1.384 (3)
C2—C4	1.532 (3)	C15—C16	1.371 (2)
C4—C5	1.533 (2)	C16—C17	1.383 (2)
C1—O1—C2	117.7 (1)	C4—C6—C7	120.2 (2)
O3—N—O4	123.3 (2)	C4—C6—C11	122.0 (1)
O3—N—C15	117.6 (2)	C7—C6—C11	117.8 (1)
O4—N—C15	119.1 (2)	C6—C7—C8	120.8 (2)
O1—C1—O2	123.8 (1)	C7—C8—C9	120.7 (2)
O1—C1—C12	111.3 (1)	C8—C9—C10	119.2 (2)
O2—C1—C12	124.9 (1)	C9—C10—C11	120.4 (2)
O1—C2—C3	106.8 (1)	C6—C11—C10	121.1 (2)
O1—C2—C4	106.5 (1)	C1—C12—C13	117.7 (1)
C3—C2—C4	114.9 (1)	C1—C12—C17	121.7 (1)
F1—C3—F2	106.2 (2)	C13—C12—C17	120.6 (1)
F1—C3—F3	106.9 (1)	C12—C13—C14	120.1 (2)
F1—C3—C2	111.9 (2)	C13—C14—C15	117.8 (1)
F2—C3—F3	106.6 (2)	N—C15—C14	117.7 (1)
F2—C3—C2	111.7 (1)	N—C15—C16	119.0 (2)
F3—C3—C2	113.1 (2)	C14—C15—C16	123.3 (1)
C2—C4—C5	111.6 (2)	C15—C16—C17	118.4 (2)
C2—C4—C6	108.9 (1)	C12—C17—C16	119.7 (1)
C5—C4—C6	112.6 (1)		

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H1···O2	1.04 (2)	2.26 (2)	2.707 (2)	104 (2)
C5—H3···F1	1.04 (2)	2.40 (2)	2.929 (2)	110 (2)
C13—H11···O3^i	1.00 (2)	2.36 (2)	3.339 (2)	167 (2)

Symmetry code: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *SDP* (B. A. Frenz & Associates Inc., 1982). Program(s) used to solve structure: *SDP*. Program(s) used to refine structure: *SDP*. Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PLATON* (Spek, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1232). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1937–1939

The Chiral Selector *N*-(2′-*S*-Hydroxypropyl)-*N*,*N*′-bis(3,5-dichlorobenzoyl)-1*R*,2*R*-diaminocyclohexane†

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Abstract

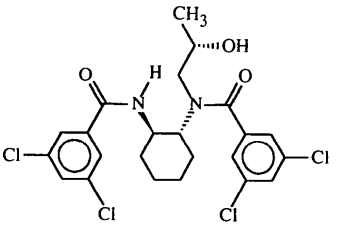
The title compound, $C_{23}H_{24}Cl_4N_2O_3$, is a chiral selector used as a stationary phase in the chromatographic separation of enantiomers. Its structure was solved by direct methods and its absolute configuration was confirmed.

Comment

Recently, much attention has been placed on the consequences of stereochemistry in biological processes. As a result, the preparation and analysis of pure enantiomers have become of increasing interest, especially in the pharmaceutical field (Ariens, 1989). The direct chromatographic separation of enantiomers represents a powerful tool for solving stereochemical problems. This technique is based on the preferential interaction of one enantiomer of a racemic compound (selectand) with a chiral discriminating agent (selector) immobilized on or adsorbed onto an inert support. Proteins, polysaccharides, cyclodextrins and synthetic polymers, as well as low molecular weight synthetic molecules, are generally used as selectors, frequently bonded to silica microparticles (Allenmark, 1991).

We have recently developed a family of chiral stationary phases (CSPs) for high-performance liquid chromatography (HPLC) applications, based on different derivatives of 1*R*,2*R*-diaminocyclohexane (DACH) (Gaparrini, Misiti & Villani, 1992). One of these CSPs, containing the *N*,*N*′-bis(3,5-dichlorobenzoyl) derivative of DACH, is particularly effective in the separation of the enantiomers of a large number of 1,2-aminoalcohols (pharmacologically active as β-blockers) in the form of oxazolidin-2-ones. It has been shown that knowledge of the recognition mechanism underlying such separations can lead to the design of improved CSPs (Pirkle, Burke & Wilson, 1989).

In this respect, we are now investigating the enantioselective interactions between a soluble model of the above CSP and the enantiomers of several racemates by a combination of physicochemical and computational techniques. Solid-state structure determination of our selector, (1), was required as a starting point for a complete conformational analysis by molecular mechanics and docking simulations with enantiomeric selectands.



(I)

The analysis of this structure does not show significant differences of bond distances and bond angles between the two molecules found in the asymmetric unit. Both have chiral N atoms quite out of plane from the corresponding cyclohexane-calculated least-squares planes. In fact, their distances from such planes are 0.75 (1), 0.002 (14), −0.33 (1) and 0.28 (1) Å for N7, N18, N107 and N118, respectively. The angle between the arylic planes is 115.6 (6) for molecule I and 128.1 (6)° for molecule II. These two molecules show slight conformational differences, mostly around one of the two N atoms. Examples of this occurrence are the torsion angles C2—N18—C19—C20 and C3—C2—N18—C19 which have values of 70 (2) and −117 (2)°, respectively, in I, while the corresponding torsion angles in II exhibit values of 97 (2) and −128 (2)°.

The two independent molecules interact with symmetry related molecules so as to form two different hydrogen bonds. The former is established by N7 with O24 of the molecule at $1-x, y-\frac{1}{2}, -z$ with a contact length of 2.92 (1) Å. The second one is due to the interaction between O22 and O122 belonging to II at $2-x, y-\frac{1}{2}, -z$ with a length of 3.00 (2) Å. Another intermolecular interaction detected in this structure determination is that involving carbonyl atoms O9, O22 and O109, and Cl

† Alternative name: (1*R*,2*R*)-2-(3,5-dichlorobenzamido)-1-{*N*-[(2*S*)-hydroxypropyl]-3,5-dichlorobenzamido}cyclohexane.