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Synthesis and Structure of New Families of Potential Antitumor or Antiviral Agents. II. 1-(*p*-Toluenesulfonyloxy)-3,4:7,8-dibenzotricyclo[3.3.2.0^{2,6}]decane

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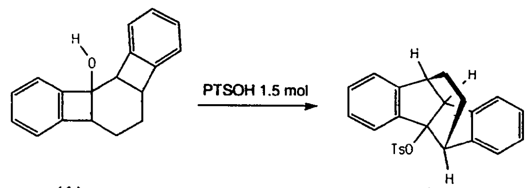
Abstract

The title compound, 3,4:7,8-dibenzotricyclo[3.3.2.0^{2,6}]-dec-1-yl *p*-toluenesulfonate was prepared by the reaction of 4b,5,6,6a,10b,10c-hexahydrobenzo[3,4]cyclobuta[1,2-*a*]biphenylen-4b-ol with an excess of *p*-toluenesulfonic acid and its structure determined by X-ray diffraction. The space group, *Cc*, is non-centrosymmetric and four chiral centres are present in the molecule (asymmetry in the environment of S also makes this atom chiral) but both enantiomers are present in the crystal as a result of the presence of the *c* glide. The conformation of the molecule is illustrated and the orientation of the *p*-toluenesulfonic substituent discussed. A systematic asymmetry of the O=S—O angles (which makes sulfur chiral) is observed.

Comment

As part of our continuing work on new families of antitumor or antiviral agents (Ianelli *et al.*, 1993), we studied the chemical behavior of 4b,5,6,6a,10b,10c-hexahydrobenzo[3,4]cyclobuta[1,2-*a*]biphenylen-4b-ol (1) in the presence of *p*-toluenesulfonic acid (PTSOH) and observed the reaction shown below.



Compound (1) remained unchanged in the presence of catalytic amounts of PTSOH, and its transformation took place only with an excess of sulfonic reagent. The structure of 1-(*p*-toluenesulfonyloxy)-3,4:7,8-dibenzotricyclo[3.3.2.0^{2,6}]decane (2), which could not be determined by classical spectroscopic methods, has been established using X-ray diffraction analysis.

A mechanism explaining the observed transformation has been proposed previously (Zouaoui *et al.*, 1991). The nucleophilic behavior of PTSOH must be emphasized; although it has been observed previously (Caubère & Mourad, 1974), such behavior is rather unusual.

It is important to note that the structure of (2), which contains a highly condensed polycyclic lipophilic part, should be of interest in obtaining potential new antivirus agents. A similar transformation is presently under investigation.

Fig. 1 shows that the molecule is built up from two fused benzocyclopentene moieties and a dimethylene bridge joining two α-C atoms of the cyclopentene rings so as to form a central cyclohexane ring fused with the benzocyclopentene cycles. The *p*-toluenesulfonyloxy substituent is inserted at an apex of the cyclohexane common to the cyclopentene rings.

The relative configurations at the C7*A*, C7*B* and C8*A* chiral centres are *R*, *S* and *R*, respectively; the enantiomer is also present in the crystal because *c* glides are present in the structure.

If the *p*-toluenesulfonyloxy substituent is not considered, there is an approximate local twofold axis running along the midpoints of bonds C8*A*—C8*B* and C9*A*—C9*B*. The most significant differences between the bonds are at C8*A* and C8*B* and therefore are probably caused by the presence of the *p*-toluenesulfonyloxy substituent. The difference (Δ/σ = 3.5) observed between the C3*A*—C4*A* and C3*B*—C4*B* benzene bonds is probably not real, but is caused instead by the high thermal motion (or disorder) affecting these atoms.

The fusion of the two benzocyclopentene systems, the presence of the dimethylene bridge and the *p*-

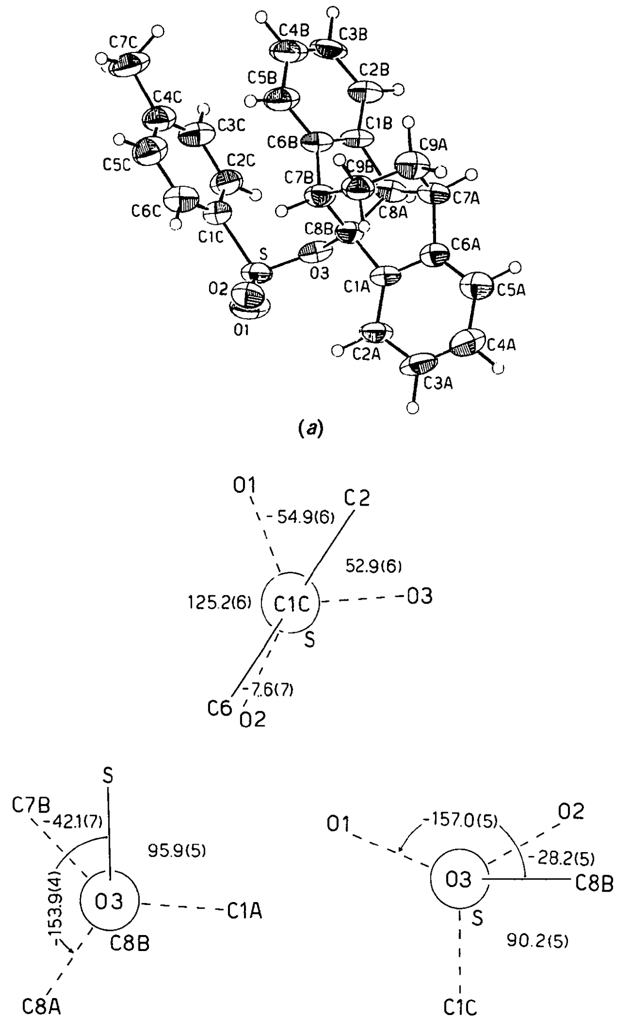


Fig. 1. (*a*) *ORTEP* drawing of the molecule with thermal ellipsoids drawn at the 50% level. (*b*) Newman projections showing the orientation of the *p*-toluenesulfonyloxy substituent.

toluenesulfonyloxy substituent have some influence on the deformations of the fused benzene rings, as shown in Table 2 where the averaged values of bond distances and angles are compared with data from the literature for the unsubstituted benzocyclopentene system (Benassi, Ianelli, Nardelli & Taddei, 1991). Significant differences and a tendency for the local mirror symmetry to be destroyed are observed. Unfortunately, the accuracy of the present analysis is not sufficient to permit a more detailed discussion of this point.

The parameters given below describe the conformation of the central fused tricyclic system where ring 1 is composed of the atoms C8*A*, C7*A*, C6*A*, C1*A*, C8*B*, ring 2 of C8*B*, C7*B*, C9*B*, C9*A*, C7*A*, C8*A*, and ring 3 of C8*B*, C7*B*, C6*B*, C1*B* and C8*A*; Q_T is the total puckering amplitude (Cremer & Pople, 1975) and ADP the asymmetry displacement parameter (Nardelli, 1983*b*). They are in agreement with the approximate local twofold symmetry.

Ring	Q_T (Å)	ADP	Conformation
1	0.452(6)	Δ_S(C8*A*) = 0.013(4)	Envelope
2	0.724(6)	Δ_2(C8*B*—C8*A*) = 0.006(3)	Distorted chair
3	0.420(6)	Δ_S(C8*B*) = 0.008(4)	Envelope

The orientation of the *p*-toluenesulfonyloxy substituent is determined mainly by intramolecular hindrance, as shown by calculations of the non-bonded potential energy when rotating fragments of that substituent about the O3—C8*B* and S—O3 directions. Indeed, the difference energy* profiles show well defined minima corresponding to the unrotated fragment. Rotation about S—C1*C* gives a minimum some 30° wide indicating that, in addition to intramolecular hindrance, electronic effects between the phenyl ring and the S atom are probably present also, as previously observed in thiosulfonic esters (Caputo, Palumbo, Nardelli & Pelizzi, 1984).

The Newman projections in Fig. 1 show that the O3—C8*B* bond (which joins the *p*-toluenesulfonyloxy substituent to the polycyclic system) is synperiplanar with respect to the S—O2 bond and antiperiplanar to S—O1, while S—O3 is synclinal to C7*B*—C8*B* and antiperiplanar to C8*B*—C8*A*. The phenyl ring is oriented so as to be synperiplanar (approximately eclipsed) with respect to the S—O2 bond, and synclinal to S—O1 and S—O3.

* Assuming that the energy corresponding to the conformation found in the crystal is zero.

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	*y*	*z*	U_{eq}
S	0.61999	0.2391 (2)	0.18490	0.0602 (6)
O1	0.6392 (4)	0.1339 (5)	0.2558 (4)	0.0801 (19)
O2	0.6641 (4)	0.3699 (5)	0.1970 (4)	0.0700 (16)
O3	0.6461 (3)	0.1635 (4)	0.0956 (3)	0.0580 (13)
C1*A*	0.7767 (4)	0.2496 (7)	0.0129 (4)	0.0557 (22)
C2*A*	0.8465 (5)	0.2736 (7)	0.0883 (4)	0.0649 (24)
C3*A*	0.9383 (5)	0.2745 (8)	0.0683 (6)	0.0764 (28)
C4*A*	0.9636 (6)	0.2582 (8)	−0.0193 (6)	0.0782 (30)
C5*A*	0.8939 (6)	0.2333 (8)	−0.0953 (5)	0.0757 (32)
C6*A*	0.8015 (5)	0.2278 (7)	−0.0747 (5)	0.0552 (23)
C7*A*	0.7135 (5)	0.2041 (8)	−0.1424 (4)	0.0623 (23)
C8*A*	0.6482 (5)	0.1412 (7)	−0.0742 (4)	0.0539 (22)
C9*A*	0.6757 (5)	0.3469 (7)	−0.1772 (5)	0.0662 (26)
C1*B*	0.5441 (4)	0.1707 (7)	−0.0981 (4)	0.0543 (21)
C2*B*	0.4751 (5)	0.0875 (8)	−0.1476 (5)	0.0690 (25)
C3*B*	0.3858 (6)	0.1438 (9)	−0.1607 (5)	0.0772 (30)
C4*B*	0.3647 (6)	0.2664 (9)	−0.1313 (5)	0.0805 (32)
C5*B*	0.4348 (5)	0.3533 (8)	−0.0815 (5)	0.0699 (25)
C6*B*	0.5234 (5)	0.2971 (7)	−0.0667 (4)	0.0542 (21)
C7*B*	0.6132 (5)	0.3656 (6)	−0.0199 (5)	0.0548 (21)
C8*B*	0.6722 (4)	0.2377 (6)	0.0109 (4)	0.0488 (17)
C9*B*	0.6598 (5)	0.4413 (7)	−0.0959 (4)	0.0654 (25)
C1*C*	0.4977 (5)	0.2599 (7)	0.1614 (4)	0.0497 (20)
C2*C*	0.4457 (5)	0.1424 (8)	0.1366 (5)	0.0646 (26)
C3*C*	0.3485 (5)	0.1597 (8)	0.1155 (5)	0.0688 (24)
C4*C*	0.3085 (5)	0.2837 (8)	0.1199 (5)	0.0645 (26)
C5*C*	0.3609 (5)	0.4000 (8)	0.1470 (5)	0.0756 (29)
C6*C*	0.4588 (5)	0.3843 (8)	0.1676 (5)	0.0692 (27)
C7*C*	0.2041 (6)	0.2983 (9)	0.0931 (6)	0.0897 (31)

Table 2. *Comparison of bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

				Average	Literature
S—O1	1.444 (5)	S—O2	1.414 (5)	1.429 (15)	1.423 (9)[a]
S—O3	1.559 (5)				1.580 (14)[a]
S—C1C	1.772 (7)				1.750 (10)[a]
O3—C8B	1.498 (8)				1.463 (17)[a]
C1A—C2A	1.416 (8)	C1B—C2B	1.409 (9)	1.413 (6)	1.388 (1)[b]
C2A—C3A	1.386 (10)	C2B—C3B	1.393 (11)	1.389 (7)	1.386 (1)[b]
C3A—C4A	1.361 (12)	C3B—C4B	1.302 (12)	1.332 (30)	1.384 (1)[b]
C4A—C5A	1.423 (11)	C4B—C5B	1.441 (11)	1.432 (9)	
C5A—C6A	1.400 (11)	C5B—C6B	1.383 (10)	1.391 (8)	
C6A—C1A	1.364 (9)	C6B—C1B	1.345 (9)	1.354 (10)	1.393 (1)[b]
C1A—C8B	1.510 (9)	C1B—C8A	1.531 (9)	1.520 (10)	
C6A—C7A	1.531 (9)	C6B—C7B	1.541 (9)	1.536 (6)	
C7A—C8A	1.557 (10)	C7B—C8B	1.535 (8)	1.544 (11)	
C7A—C9A	1.544 (10)	C7B—C9B	1.532 (10)	1.538 (7)	
C8A—C8B	1.546 (8)	C9A—C9B	1.520 (10)	1.536 (13)	
C1C—C2C	1.384 (10)	C4C—C5C	1.385 (11)	1.384 (7)	1.388 (13)[a]
C1C—C6C	1.331 (10)	C3C—C4C	1.331 (11)	1.331 (7)	1.375 (14)[a]
C2C—C3C	1.413 (10)	C5C—C6C	1.419 (10)	1.416 (7)	1.377 (12)[a]
C4C—C7C	1.520 (11)				1.504 (20)[a]
O3—S—C1C	102.8 (3)				103.2 (19)[a]
S—O3—C8B	123.7 (3)				119.6 (24)[a]
O1—S—C1C	108.9 (3)	O2—S—C1C	110.3 (3)	109.6 (7)	109.4 (9)[a]
O1—S—O3	102.1 (3)				104.3 (16)[a]
O2—S—O3	111.8 (3)				109.4 (8)[a]
O1—S—O2	119.4 (3)				119.8 (8)[a]
C6A—C1A—C8A	109.5 (5)	C6B—C1B—C8A	110.0 (6)	109.7 (4)	110.4 (1)[b]
C2A—C1A—C8B	130.6 (5)	C2B—C1B—C8A	128.9 (6)	129.9 (8)	128.9 (4)[b]
C2A—C1A—C6A	119.8 (6)	C2B—C1B—C6B	121.0 (6)	120.4 (6)	120.6 (6)[b]
C1A—C2A—C3A	117.2 (6)	C1B—C2B—C3B	116.0 (7)	116.7 (6)	118.6 (2)[b]
C2A—C3A—C4A	123.6 (7)	C2B—C3B—C4B	123.8 (8)	123.7 (5)	120.8 (2)[b]
C3A—C4A—C5A	119.5 (8)	C3B—C4B—C5B	120.8 (8)	120.2 (6)	
C4A—C5A—C6A	116.9 (7)	C4B—C5B—C6B	115.8 (7)	116.4 (6)	
C1A—C6A—C5A	123.0 (6)	C1B—C6B—C5B	122.6 (6)	112.8 (4)	
C5A—C6A—C7A	127.9 (6)	C5B—C6B—C7B	128.2 (6)	128.0 (4)	
C1A—C6A—C7A	109.1 (6)	C1B—C6B—C7B	109.1 (6)	109.1 (4)	
C6A—C7A—C8A	100.0 (5)	C6B—C7B—C8B	101.3 (5)	100.6 (6)	
C6A—C7A—C9A	108.2 (5)	C6B—C7B—C9B	107.8 (5)	108.0 (4)	
C8A—C7A—C9A	109.6 (6)	C8B—C7B—C9B	108.4 (5)	108.9 (6)	
C7A—C8A—C8B	99.6 (5)	C7B—C8B—C8A	100.7 (5)	100.2 (6)	
C7A—C8A—C1B	115.7 (5)				
C7B—C8B—C1A	117.8 (5)				
C1B—C8A—C8B	101.2 (5)	C1A—C8B—C8A	101.3 (5)	101.2 (4)	
C7A—C9A—C9B	111.2 (5)	C7B—C9B—C9A	112.3 (5)	111.8 (6)	
O3—C8B—C7B	115.9 (5)				
O3—C8B—C8A	107.7 (5)				
O3—C8B—C1A	111.2 (5)				
S—C1C—C6C	120.5 (5)	S—C1C—C2C	117.2 (5)	118.8 (16)	119.8 (9)[a]
C2C—C1C—C6C	122.3 (7)				120.3 (10)[a]
C1C—C2C—C3C	117.1 (7)	C1C—C6C—C5C	119.9 (7)	118.5 (14)	119.3 (8)[a]
C2C—C3C—C4C	121.4 (7)	C4C—C5C—C6C	118.3 (7)	119.8 (15)	121.6 (8)[a]
C3C—C4C—C5C	120.9 (7)				117.9 (9)[a]
C3C—C4C—C7C	119.6 (7)	C5C—C4C—C7C	119.5 (7)	119.6 (5)	121.0 (12)[a]

Notes: (*a*) averaged values from 58 *p*-$CH_3.C_6H_4.SO_2.O.C(sp^3)$ fragments with $R1 < 0.07$ and $\sigma[d(C—C)] < 0.01$ Å retrieved from the Cambridge Structural Database (Allen *et al.*, 1979); (*b*) values from Benassi *et al.* (1991).

It is interesting to note that there is a significant difference between the angles O1—S—O3 and O2—S—O3 (Δ = 9.7°; Δ/σ = 22.9); this kind of asymmetry, which makes the S atom chiral, seems peculiar to this part of the substituent, as shown by the averaged data from the literature (July 1992 release of the Cambridge Structural Database; Allen *et al.*, 1979) quoted in Table 2. The same kind of asymmetry has been observed in thiosulfonic esters (Caputo *et al.*, 1984) and in *N*-sulfonylsulfilimines containing the *R*—SO_2—N= system (Kálmán, Parkanyi & Kucsman, 1980).

Packing is determined only by van der Waals contacts.

Experimental

Crystal data

$C_{25}H_{22}O_3S$
M_r = 402.51
Monoclinic
Cc
a = 14.434 (6) Å
b = 9.637 (2) Å
c = 14.398 (7) Å
β = 96.34 (2)°
V = 1991 (1) Å^3
Z = 4
D_x = 1.343 Mg m^{-3}

Cu $K\alpha_1$ radiation
λ = 1.540562 Å
Cell parameters from 29 reflections
θ = 20.08–39.38°
μ = 1.592 mm^{-1}
T = 293 (2) K
Small prisms
0.39 × 0.28 × 0.23 mm
Colorless

Data collection

Siemens-AED diffractometer	$\theta_{max} = 70.20°$
θ-2θ scans	$h = -10 \rightarrow 17$
Absorption correction: none	$k = 0 \rightarrow 11$
	$l = -17 \rightarrow 17$
3676 measured reflections	1 standard reflection monitored every 50 reflections
2534 independent reflections	intensity variation: within statistical fluctuation
1423 observed reflections $[I > 2\sigma(I)]$	
$R_{int} = 0.0986$	

Refinement

Final $R1 = 0.0655$ for $F_o > 4\sigma(F_o)$	Extinction correction: $F_c^* = kF_c[1+(0.001 \times F_c^2\lambda^3)/\sin(2\theta)]^{-1/4}$
$wR2 = 0.1519$ for F^2 data	Extinction coefficient: $k = 0.0015$ (2)
$S = 0.864$ for all F^2 data	Atomic scattering factors from *International Tables for X-ray Crystallography* [1974, Vol. IV, Tables 2.2A, 2.3.1 (S, O, C) and 2.2C (H)]
2516 reflections	
266 parameters	
Calculated weights $w = 1/[\sigma^2(F_o^2)+(0.0676P)^2]$ where $P = (F_o^2+2F_c^2)/3$	
$(\Delta/\sigma)_{max} = 0.002$	
$\Delta\rho_{max} = 0.437$ e Å^{-3}	
$\Delta\rho_{min} = -0.368$ e Å^{-3}	

Refinement on F^2 for all reflections except those flagged for possible systematic errors; the observed threshold $I > 2\sigma(I)$ is used only for calculating R(obs.) *etc.* given here for comparison with refinements on F.

Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1986). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1992). Molecular graphics: *ORTEP* (Johnson, 1965). Software used for geometric calculations: *PARST* (Nardelli, 1983*a*). Software used to prepare material for publication: *PARST*. The calculations were performed using the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma).

The integrated intensities were measured using a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure. A correction for Lorentz and polarization effects was applied.

The structure was determined by direct methods with *SHELXS*86 and refined by anisotropic full-matrix least squares on F using *SHELX*76 and on F^2 (to have a better ratio between the number of observations and the number of refined parameters) using *SHELXL*92. The values of the conventional residual-error indices at the end of the F refinement were $R = 0.0702$, $wR = 0.0820$ and $S = 0.930$ for 1428 reflections and 336 refined parameters, while the residual indices obtained in the F^2 refinement had the values $wR2$ $(= \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}) = 0.1519$ for 2516 independent reflections and 266 parameters, $S = 0.864$ and $wR2 = 0.1849$ for all 2534 reflections (18 reflections with $\Delta/\sigma > 5$ omitted), $S = 1.083$ and $R1$ $[= \Sigma|F_o-F_c|/\Sigma(F_o)] = 0.0655$ for 1423 reflections with $F_o > 4\sigma(F_o)$. The absolute structure was determined on the basis of the Flack (1983) parameter $x = -0.01$ (4).

As expected, the e.s.d.'s from the F^2 analysis are lower than those from the refinement on F because of the larger number of observations and the reduced number of parameters. A further comparison of the results of the two kinds of analysis considered the half-normal probability plot (Abrahams & Keve, 1971) calculated using the program *ABRAHAMS* (Gilli, 1977) for all interatomic distances < 4.65 Å (excluding those involving H atoms) according to De Camp (1973). The parameters of the regression line through the distribution of points in the plot [intercept 0.033 (3), slope 0.687 (3), correlation coefficient $r = 0.997$, $N = 225$] indicate that there are no significant systematic effects and that the pooled standard deviations are overestimated by a factor of about 1.5. In agreement with this finding, no significant differences (*i.e.* $> 3\Delta/\sigma$) are observed for the structural parameters (distances, angles, torsions) derived from the two analyses.

The same analysis performed on the equivalent isotropic atomic displacement parameters gives a plot in which the regression-line parameters [intercept 0.000 (1), slope 0.037 (1), correlation coefficient $r = 0.986$, $N = 29$] show that the pooled standard deviations are overestimated. This is a consequence of the fact that the differences between the U_{eq} values from the two refinements are much smaller than their e.s.d.'s.

The anisotropic atomic displacements, analysed in terms of the **LST** rigid-body model (Schomaker & Trueblood, 1968; Trueblood, 1978) gave a residual index R_{wU} $\{= [\Sigma(w\Delta U)^2/\Sigma(wU_o)^2]^{1/2};\ \Delta U = U_{ij}(\text{obs.})-U_{ij}(\text{calc.})\} = 0.127$ which improved to 0.100 by considering the internal motions according to Dunitz & White (1973). The atoms most affected by these motions (or static disorder) are C3*A*, C3*B*, C4*B* and C7*C*, which also show the greatest anisotropies with ratios between the maximum and minimum axes of the displacement ellispsoids larger than 4. These calculations were performed using the *THMV* program (Trueblood, 1984).

All the structural parameters discussed in the *Comment* are from the F^2 refinements.

The authors are indebted to Professor G. M. Sheldrick who kindly made his program *SHELXL*92 available to them at the beta-test stage. Financial support from the European Community Commission under contract No. SC1000657 is gratefully aknowledged.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry together with statistics and CSD bibliographic references for the *p*-toluenesulfonyloxy substituent have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55927 (46 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1032]

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Synthesis and Structure of Strained Polycyclic Cyclobutane-Containing Derivatives

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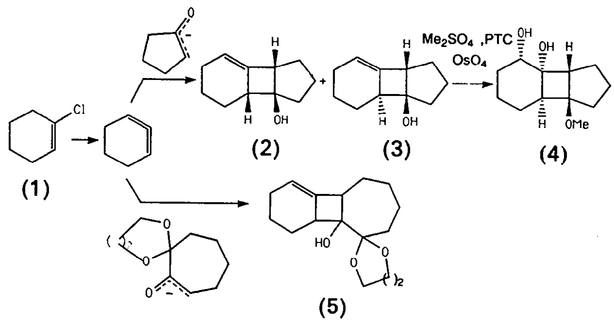
Abstract

The compounds *cis,anti,cis*-8-methoxytricyclo[6.3.0.-$0^{2,7}$]undecan-2,3-diol and *cis,anti,cis*-tricyclo[6.5.0.$0^{2,7}$]-tridec-6-en-13-spiro-2′-[1,3]dioxan-1-ol were obtained by condensation of ketone enolates with cyclohexadiene generated *in situ* from 1-chlorocyclohexene. X-ray structure analysis established the conformations of the polycyclic systems, the stereochemistry at the ring junctions and the deformations caused by fusion of the rings. The results of the refinements on F and F^2 are compared.

Comment

It was shown for the first time in a work by Caubère & Brunet (1972) that condensation of a ketone enolate with cyclohexadiene, generated *in situ* from 1-chlorocyclohexene, leads easily to the synthesis of a methylene cyclobutenol with *cis,syn,cis* structure. Returning to these reactions with the object of finding a new route to polycyclic cyclopentane derivatives, we performed the reactions shown in the scheme below (PTC = phase transfer catalysis).



Compound (3) has not been obtained previously and its formation can be attributed to the new experimental conditions used here (a temperature lower than 273 K and dimethoxyethane). It was first transformed into the corresponding ether which was bishydroxylated into compound (4) (Minato, Yamamoto & Tsuji, 1990) whose structure could only be established by X-ray analysis. Using this knowledge, it was possible to infer the structure of (3).

Another reaction we considered was the condensation of the enolate of cycloheptanedione monoketal; although this reaction is much less easy than arynic condensation (Grégoire, Carré & Caubère, 1986), we succeeded in obtaining compound (5) whose stereochemistry could not be determined easily from classical spectroscopic data and was therefore defined by X-ray analysis.

The present paper reports the structures of compounds (4) and (5) which are good starting materials for further transformations (Jamart-Grégoire, Brosse, Caubère, Ianelli & Nardelli, 1991), for example those of (5) into the rearranged polycyclic derivatives we are currently investigating.

The *ORTEP* (Johnson, 1965) projections (Fig. 1) show that both molecules are built up of a tricyclic core with an *anti* conformation and with *cis* configurations at the

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