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An Octahydro-3a,6-methanoazulen-5-one Resulting from an Intramolecular Friedel–Crafts Acylation

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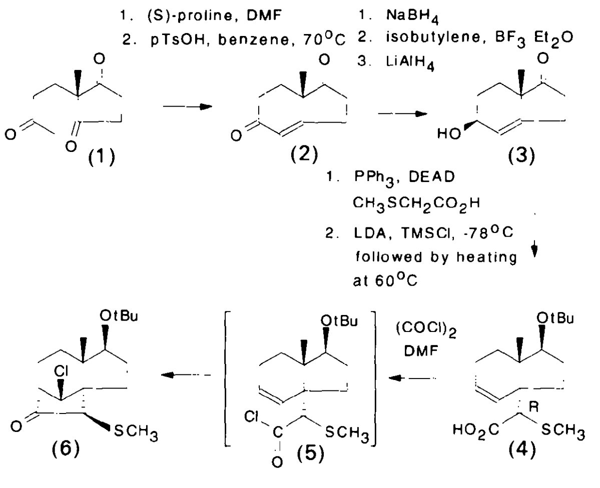
Abstract

The compound (1*S*,3a*R*,4*R*,6*S*,8a*S*,9*S*)-1-*tert*-butoxy-9-chloro-2,3,3a,4,6,7,8,8a-octahydro-8a-methyl-4-methylthio-1*H*-3a,6-methanoazulen-5-one, $C_{17}H_{27}ClO_2S$, was identified as the reaction product when the acid chloride formed from a *trans*-fused perhydroindane derivative underwent a Friedel-Crafts acylation of the internal olefin.

Comment

As part of a program to synthesize the *C* and *D* rings of the cucurbitanes (see Richardson, Sabol & Watt, 1989), the proline-catalyzed cyclization of the prochiral triketone (1) was employed to secure the enone (2) in high enantiomeric excess and good yield (see Hajos & Parrish, 1974). Successive reduction and protection of the non-conjugated carbonyl in (2) was followed by reduction of the conjugated carbonyl to afford the allylic alcohol (3). A Mitsunobu inversion with (methylthio)acetic acid set the stage for a Claisen rearrangement that led to the substituted *trans*-fused perhydroindane skeleton in the intermediate carboxylic acid (4) (Richardson *et al.*, 1989). At this stage, the carboxylic acid functionality in (4) was superfluous and methods for removing this one-carbon unit were investigated. In order to achieve the decarboxylation of (4), derivatives of the carboxylic acid (*e.g.* the phenylseleno ester) were examined. Preparation of the esters required the activation of the carboxylic acid as the acid chloride but the intermediate acid chloride (5)



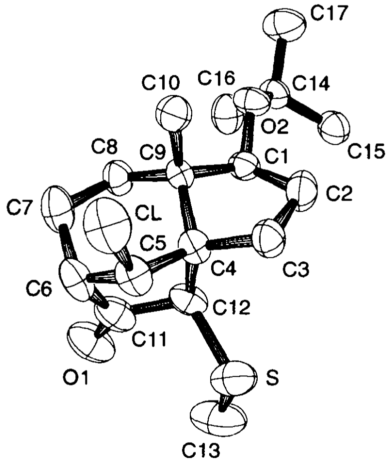


Fig. 1. Perspective drawing of the molecular structure of TRICYC showing the atom-numbering scheme. The shapes of the ellipsoids correspond to 50% probability contours of atomic displacement. The H atoms have been omitted for clarity.

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underwent an unexpected Friedel-Crafts acylation of the internal olefin to afford the tricyclic ketone (6) as the principal product. The identity and absolute configuration of (6) (hereafter abbreviated to TRICYC) were determined in this X-ray diffraction study.

The bond lengths and angles of TRICYC are normal (Allen *et al.*, 1987).

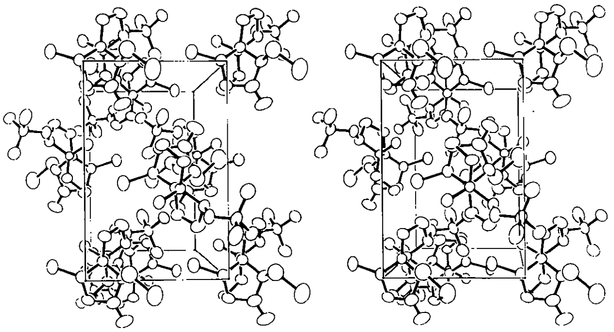

Fig. 2. Stereoscopic drawing of the unit cell of TRICYC. The *c* axis points from left to right, the *a* axis points downwards and the *b* axis points into the plane of the paper.

Experimental

Crystal data

$C_{17}H_{27}ClO_2S$
M_r = 330.9
Orthorhombic
$P2_12_12_1$
a = 12.281 (1) Å
b = 17.844 (1) Å
c = 8.076 (1) Å
V = 1769.8 (3) Å^3
Z = 4
D_x = 1.242 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 9.1-34.9°
μ = 3.026 mm^{-1}
T = 295 (1) K
Thick plates
0.50 × 0.33 × 0.28 mm
Colorless

Data collection

Enraf-Nonius CAD-4*VAX* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min}$ = 0.331, $T_{\max}$ = 0.633
1513 measured reflections
1513 independent reflections
1457 observed reflections [$I > 3\sigma(I)$]

$\theta_{\max}$ = 60.0°
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity variation: 3.9%
Some reflections with $|h|>8$ were measured for h, k and l all negative

Refinement

Refinement on F
R = 0.042
wR = 0.057
S = 3.33

Extinction correction: Zachariasen (1968)
Extinction coefficient: 6.5 (7) × 10^{-8}

1457 reflections
191 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max}$ = 0.10
$\Delta\rho_{\max}$ = 0.19 e Å^{-3}
$\Delta\rho_{\min}$ = −0.30 e Å^{-3}

Atomic scattering factors from *International Tables for X-ray Crystallography* [Vol. IV, Tables 2.2A (Cl, S, O, C, H) and 2.3.1 (Cl, S)]
Absolute configuration: based on refinements of the two enantiomers (Rogers, 1981)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cl	−0.05596 (10)	0.05920 (7)	−0.23562 (13)	5.68 (3)
S	−0.04006 (11)	−0.06926 (6)	0.29844 (17)	5.88 (3)
O1	0.1922 (3)	0.02241 (18)	0.2661 (5)	6.5 (1)
O2	−0.1935 (2)	0.23395 (13)	0.2998 (3)	3.8 (1)
C1	−0.1533 (3)	0.1591 (2)	0.2869 (5)	3.4 (1)
C2	−0.2446 (3)	0.1005 (2)	0.2583 (6)	4.6 (1)
C3	−0.1993 (3)	0.0439 (2)	0.1339 (6)	4.1 (1)
C4	−0.0791 (3)	0.0628 (2)	0.1171 (5)	3.3 (1)
C5	−0.0119 (3)	0.0337 (2)	−0.0296 (5)	4.0 (1)
C6	0.1018 (3)	0.0599 (2)	0.0126 (6)	4.5 (1)
C7	0.1119 (3)	0.1459 (3)	0.0192 (6)	5.1 (1)
C8	0.0371 (3)	0.1798 (2)	0.1511 (5)	3.8 (1)
C9	−0.0794 (3)	0.1506 (2)	0.1329 (4)	2.8 (1)
C10	−0.1349 (3)	0.1908 (2)	−0.0120 (5)	4.1 (1)
C11	0.1095 (3)	0.0337 (2)	0.1906 (6)	4.8 (1)
C12	−0.0058 (3)	0.0288 (2)	0.2577 (6)	4.0 (1)
C13	0.0520 (6)	−0.0904 (3)	0.4658 (7)	8.1 (2)
C14	−0.2012 (3)	0.2659 (2)	0.4638 (5)	3.7 (1)
C15	−0.2662 (3)	0.2161 (2)	0.5796 (5)	4.6 (1)
C16	−0.0886 (4)	0.2798 (3)	0.5318 (6)	5.6 (1)
C17	−0.2601 (4)	0.3396 (2)	0.4324 (6)	5.8 (1)

Table 2. *Geometric parameters* (Å, °)

Cl—C5	1.807 (4)	C4—C12	1.571 (5)
S—C12	1.830 (4)	C5—C6	1.512 (5)
S—C13	1.802 (6)	C6—C7	1.542 (6)
O1—C11	1.203 (5)	C6—C11	1.514 (7)
O2—C1	1.428 (4)	C7—C8	1.531 (5)
O2—C14	1.445 (4)	C8—C9	1.530 (5)
C1—C2	1.549 (5)	C9—C10	1.533 (5)
C1—C9	1.547 (5)	C11—C12	1.518 (6)
C2—C3	1.530 (6)	C14—C15	1.516 (5)
C3—C4	1.521 (5)	C14—C16	1.508 (6)
C4—C5	1.533 (5)	C14—C17	1.523 (5)
C4—C9	1.572 (5)		
C12—S—C13	101.0 (3)	C7—C8—C9	111.1 (3)
C1—O2—C14	117.3 (3)	C1—C9—C4	99.5 (3)
O2—C1—C2	113.1 (3)	C1—C9—C8	116.0 (3)
O2—C1—C9	110.7 (3)	C1—C9—C10	107.8 (3)
C2—C1—C9	103.8 (3)	C4—C9—C8	110.2 (3)
C1—C2—C3	106.3 (3)	C4—C9—C10	113.9 (3)
C2—C3—C4	105.3 (3)	C8—C9—C10	109.3 (3)
C3—C4—C5	121.1 (3)	O1—C11—C6	125.9 (5)
C3—C4—C9	102.2 (3)	O1—C11—C12	126.7 (5)
C3—C4—C12	114.0 (3)	C6—C11—C12	107.4 (4)
C5—C4—C9	113.6 (3)	S—C12—C4	111.5 (3)
C5—C4—C12	96.9 (3)	S—C12—C11	109.5 (3)
C9—C4—C12	109.1 (3)	C4—C12—C11	104.7 (4)
Cl—C5—C4	117.7 (3)	O2—C14—C15	111.6 (3)
Cl—C5—C6	114.0 (3)	O2—C14—C16	109.8 (3)
C4—C5—C6	102.6 (3)	O2—C14—C17	102.7 (3)
C5—C6—C7	112.9 (3)	C15—C14—C16	110.8 (3)
C5—C6—C11	100.2 (4)	C15—C14—C17	111.0 (3)
C7—C6—C11	105.6 (4)	C16—C14—C17	110.7 (4)
C6—C7—C8	111.6 (4)		

The product is the result of the reaction of compound (7*a*) of Richardson *et al.* (1989) with $(COCl)_2$. Analytical data: IR

(KBr) 1752 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.12 [*s*, 9, $C(CH_3)_3$], 1.30 (*s*, 3, angular CH_3), 2.27 (*s*, 3, SCH_3), 3.59–3.67 [*m*, 1, C*H*OC(CH_3)$_3$], 4.75 (*d*, *J* = 4.6 Hz, 1, CHCl); ^{13}C NMR ($CDCl_3$) δ 15.3, 17.6, 21.8, 23.6, 28.7, 29.9, 30.0, 47.3, 52.0, 56.3, 56.8, 60.5, 72.8, 94.1, 209.0. Elemental analysis for $C_{17}H_{27}ClO_2S$: calculated C 61.70, H 8.22%; found C 61.62, H 8.35%.

Most of the reflections from TRICYC correspond to the orthorhombic space group $P2_12_12_1$ but a small number appear to define a monoclinic supercell. The two cells are related by the matrix equation $a_{\rm monoclinic}$ = (1 0 1 / 0 1 0 / −1 0 2) $a_{\rm orthorhombic}$; the constants of the larger ($V_{\rm monoclinic} = 3V_{\rm orthorhombic}$) monoclinic cell are *a* = 14.694 (2), *b* = 17.837 (2), *c* = 20.278 (1) Å and β = 93.96 (1)°. Data corresponding to the smaller cell were measured at Enraf-Nonius in New York. Data for the apparent supercell were also collected for a quadrant of reciprocal space having $2\theta < 50°$, but, of the 3924 reflections having $h + l \neq 3n$, only 30 had $I > 3\sigma(I)$. Since there are no indications in the anisotropic displacement parameters of the fully refined structure (see Figs. 1 and 2) of disorder or of any unusual patterns, it is possible that the extra reflections correspond to a second (and much smaller) individual of a twin. The diffraction patterns of three other crystals from the same batch could not be indexed automatically, presumably because they were twins.

All calculations were performed at the University of Kentucky. As part of the data processing, intensities of reflections having $I < 3\sigma(I)$ were set equal to zero if the only counts available were for the fast (10.2° min^{-1} in ω) prescan. The Cl and S atoms were located using the *MULTAN77* direct-methods package (Main, Lessinger, Woolfson, Germain & Declercq, 1977); the remainder of the molecule was then revealed by the *DIRDIF* program (Beurskens *et al.*, 1983). Methyl H atoms could be located in difference Fourier maps. The H atoms were idealized at a late point in the refinement and added as fixed contributions (C—H = 1.00 Å; *B* values 1 Å^2 greater than $B_{\rm eq}$ of the attached C atom). Inclusion of an isotropic extinction coefficient improved the agreement factor *R* from 0.047 to 0.042 {extinction correction: $k|F_c| = F_o[x^* + (1 + x^{*2})^{1/2}]^{1/2}$, where $x^* = (EC)\beta I_{\rm int}$; the value of *EC* is refined, $\beta = [1 + \cos^2(2\theta_{\rm monoclinic})] \times [1 + \cos^2(2\theta_{\rm monoclinc})\cos^4(2\theta)]/[1 + \cos^2(2\theta_{\rm monoclinic})\cos^2(2\theta)]^2$, and $I_{\rm int}$ is the integrated intensity before correction for Lorentz and polarization effects; see equations (3) and (4) of Zachariasen (1968)}. The absolute chirality was assigned on the basis of refinements of the two enantiomers and was consistant with the synthetic pathway; the ratio of the *wR* factors for the two enantiomers is 1.32 (*R* = 0.054, *wR* = 0.075, *S* = 4.37 for the other enantiomer), which means that the enantiomer choice is essentially certain [*N* = 1266 and $\alpha < 1 \times 10^{-4}$ (Rogers, 1981)]. The largest peaks and deepest troughs in the final difference map are associated with the S and Cl atoms and with the centers of the C—C bonds.

Data collection: *CAD*-4*VAX* (Enraf-Nonius, 1988). Cell refinement: *CAD*-4*VAX*. Data reduction: local program (Brock). Program(s) used to refine structure: local program based on Ibers's version of *ORFLS* (Busing, Martin & Levy, 1962). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *ORFFE* (Busing, Martin & Levy, 1964) and a local program (Brock).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71444 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR1062]

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Structure of a Cyclophane Containing a 1,5,2,4,6,8-Dithiatetrazocine Ring

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Abstract

(*N*,*N*′-Dimethyl-*N*,*N*′-octamethylene-3,7-diamino)-1,5,2,4,6,8-dithiatetrazocine, $C_{12}H_{22}N_6S_2$, is the first cyclophane to contain the dithiatetrazocine ring system. The heterocycle is sharply folded, with a dihedral angle of 101.8°, along an axis drawn through the two S atoms. The bridging octamethylene chain passes over one side, rather than over the center, of the heterocyclic ring.

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