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Novel Products from the Rearrangement of Some [*n*.3.1]Propellanes

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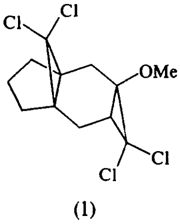
Abstract

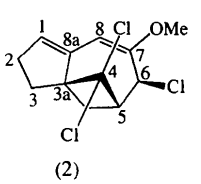
The title compounds, (3aα,5α,6α)-4,4,6-trichloro-7-methoxy-3,4,5,6-tetrahydro-2*H*-3a,5-methanoazulene and (3aα,6α)-(*E*)-8,8-dichloro-5-chloromethylene-6-methoxy-1,2,3,4,5,6-hexahydro-3a,6-methano-3a*H*-indene, both $C_{12}H_{13}Cl_3O$, were formed by mild thermolyses of two related [4.3.1]propellanes and are of interest in the development of new methods for preparing novel analogues of the anti-cancer drug Taxol™.

Comment

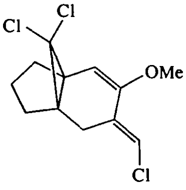
As part of a program directed towards exploiting *gem*-dihalogeno[*n*.*m*.1]propellanes in chemical synthesis (Banwell, Gable, Peters & Phyland, 1995; Banwell & Schuhbauer, 1997), we had occasion to study the response of compounds (1) and (3) to mild thermolytic conditions. The conversion of (1) to (2), possessing a rearranged skeleton as determined by NMR analysis, was observed. The conversion of (3) to (4) by an as yet undetermined pathway involving skeletal rearrangement was also observed. These thermally induced conversions are, to the best of our knowledge, unprecedented, so we sought proof by undertaking the X-ray analyses of the rearrangement products (2) and (4).



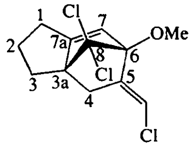
(1)



(2)



(3)



(4)

The molecular structure of (2) is illustrated in Fig. 1(*a*) (see also Table 1). The cyclopentene ring does not adopt the expected envelope conformation, the ring atoms being coplanar to within 0.028 (5) Å (r.m.s. deviation 0.021 Å). The cyclopentene ring adopts a fairly regular sofa form with atoms C3a, C8a, C8, C7, C6 and C5 coplanar to within 0.021 (4) Å (r.m.s. deviation 0.015 Å), and atom C4 lying 1.055 (8) Å from the plane. The mean plane through the cyclobutane ring atoms (mean deviation 0.142 Å) is almost orthogonal to both the cyclopentene ring and the six-atom plane of the cycloheptene ring at angles of 89.2 (3) and 87.8 (2)°, respectively. The inter-bond angles in the cyclobutane ring range from 86.9 (5) to 89.2 (5)°.

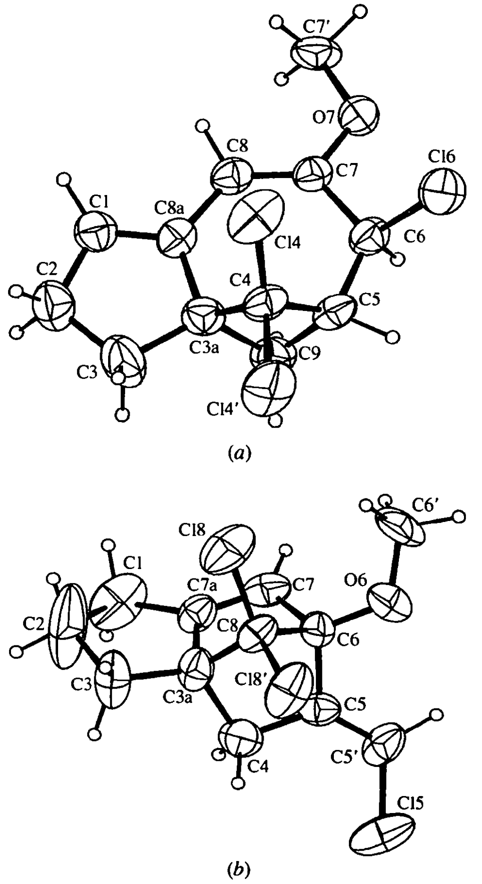


Fig. 1. Perspective views of (*a*) the 3a*R*,5*S*,6*S* enantiomer of (2) and (*b*) the 3a*R*,6*S* enantiomer of (4), with displacement ellipsoids scaled to 50% probabilities. The H atoms are denoted by spheres of arbitrary radii.

The molecular structure of (4) is shown in Fig. 1(*b*) (see also Table 2). The cyclopentane ring is constrained to a form between a half chair and an envelope as indicated by the pseudo-rotation parameters (Altona, Geise & Romers, 1968) Δ = 18.7 and φ_m = 25.1°. This conformation no doubt arises as a consequence of the C_{sp^2} ring atom C7a. The cyclohexene ring is a fairly regular boat as shown by the conformational asymmetry parameter (Duax & Norton, 1975) Δ_s^{2a} = 2.4°. The two five-membered rings formed by the C8 bridge from C3a to C6 are, as expected, envelope, with C8 out-of-plane of the other four ring atoms (pseudo-rotational parameters are $\Delta = 36.4$, $\varphi_m = 55.8°$ and $\Delta = 32.0$, $\varphi_m = 58.1°$). The angles subtended at C7a are distorted from the regular trigonal value, the exocyclic angle C1—C7a—C7 having expanded by 20° and the two endocyclic angles having contracted by 10°. One bridging bond across the cyclohexene ring, C6—C8 of 1.592 (6) Å, is 0.05 Å larger than the regular C_{sp^3}—C_{sp^3} value, and five of the inter-bond angles involving bridging atom C8 are significantly less than the regular tetrahedral value and range in value from 92.9 (3) to 101.3 (3)°.

Experimental

A 0.08 *M* solution of compound (1) (Banwell, Gable, Peters & Phyland, 1995) in 2,6-lutidine (b.p. 416–418 K) was heated at reflux for 48 h, then cooled to room temperature and partitioned between dichloromethane and water. The separated organic phase was washed with saturated aqueous $CuSO_4$ and then water before being dried ($MgSO_4$), filtered and concentrated under reduced pressure. The yellow–brown oil obtained in this way was subjected to preparative thick-layer chromatography (silica gel, 5:95 ethyl acetate/hexane elution) and the single major and chromophoric band (R_f = 0.3) was extracted to give a white solid of compound (2) which crystallized from ethanol. A 0.1 *M* solution of compound (3) (Banwell, Gable, Halton & Phyland, 1995) in 2,6-lutidine was heated at reflux for 60 h, then cooled to room temperature and worked up in the same manner as described above. The yellow oil thus obtained was taken up in methanol and the resulting solution cooled to 258 K, thereby providing crystals of compound (4).

Compound (2)

Crystal data

$C_{12}H_{13}Cl_3O$
$M_r = 279.59$
Orthorhombic
$Pna2_1$
$a = 6.805\,(1)$ Å
$b = 13.225\,(1)$ Å
$c = 13.902\,(1)$ Å
$V = 1251.1\,(2)$ Å^3
$Z = 4$
$D_x = 1.484$ Mg m^{-3}
$D_m = 1.47\,(1)$ Mg m^{-3}
D_m measured by flotation in $K_2[HgI_4]$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 19$–$37°$
$\mu = 6.43$ mm^{-1}
$T = 292\,(2)$ K
Prismatic
0.173 × 0.109 × 0.071 mm
Colourless

Data collection

Rigaku AFC diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*SHELX76*; Sheldrick, 1976)
$T_{min} = 0.283$, $T_{max} = 0.479$
1069 measured reflections
1069 independent reflections

942 reflections with $I > 2\sigma(I)$
$\theta_{max} = 65°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 16$
3 standard reflections every 50 reflections intensity decay: <1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.125$
$S = 1.031$
1069 reflections
145 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0758P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$

$\Delta\rho_{max} = 0.401$ e Å^{-3}
$\Delta\rho_{min} = -0.336$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.05 (4)

Table 1. *Selected geometric parameters (Å, °) for (2)*

C1—C2	1.478 (10)	C4—Cl4′	1.808 (6)
C1—C8a	1.345 (8)	C5—C6	1.511 (8)
C2—C3	1.528 (11)	C5—C9	1.558 (9)
C3—C3a	1.524 (9)	C6—C7	1.505 (8)
C3a—C4	1.556 (9)	C6—Cl6	1.838 (6)
C3a—C8a	1.494 (8)	C7—O7	1.365 (7)
C3a—C9	1.543 (8)	C7—C8	1.340 (8)
C4—C5	1.544 (8)	O7—C7′	1.435 (8)
C4—Cl4	1.771 (6)	C8—C8a	1.472 (8)
C2—C1—C8a	112.9 (6)	C4—C5—C6	118.8 (5)
C1—C2—C3	104.0 (6)	C4—C5—C9	86.9 (5)
C2—C3—C3a	107.5 (6)	C6—C5—C9	113.1 (5)
C3—C3a—C4	121.6 (6)	C5—C6—C7	119.9 (5)
C3—C3a—C8a	104.2 (5)	C5—C6—Cl6	108.8 (4)
C3—C3a—C9	119.9 (6)	C7—C6—Cl6	110.0 (4)
C4—C3a—C8a	112.1 (5)	C6—C7—C8	128.0 (5)
C4—C3a—C9	87.0 (5)	O7—C7—C8	123.5 (5)
C8a—C3a—C9	111.5 (5)	C6—C7—O7	108.2 (5)
C3a—C4—C5	89.2 (4)	C7—O7—C7′	117.9 (5)
C3a—C4—Cl4	118.3 (5)	C7—C8—C8a	127.8 (5)
C3a—C4—Cl4′	111.5 (4)	C1—C8a—C8	123.0 (5)
C5—C4—Cl4	121.3 (4)	C1—C8a—C3a	111.2 (5)
C5—C4—Cl4′	108.6 (4)	C3a—C8a—C8	125.7 (4)
Cl4—C4—Cl4′	107.0 (3)	C3a—C9—C5	89.2 (5)
C1—C2—C3—C3a	3.9 (9)	C8a—C3a—C9—C5	91.9 (5)
C2—C3—C3a—C8a	−4.8 (8)	C6—C5—C9—C3a	−99.2 (5)
C3—C3a—C8a—C1	4.0 (7)	C9—C3a—C4—Cl4	146.5 (4)
C3a—C8a—C1—C2	−1.6 (7)	C9—C3a—C4—Cl4′	−88.9 (4)
C8a—C1—C2—C3	−1.5 (8)	C9—C3a—C4—C5	20.9 (4)
C3a—C4—C5—C6	94.0 (6)	C3—C3a—C4—C5	144.6 (7)
C4—C5—C6—C7	−47.2 (8)	C6—C5—C4—Cl4	−29.1 (8)
C5—C6—C7—C8	−2.5 (9)	C3—C3a—C9—C5	−146.0 (6)
C6—C7—C8—C8a	1.7 (9)	C3—C3a—C4—Cl4′	34.6 (6)
C7—C8—C8a—C3a	−2.7 (9)	C4—C5—C6—Cl6	80.5 (6)
C8—C8a—C3a—C4	50.8 (7)	Cl6—C6—C7—O7	56.7 (5)
C8a—C3a—C4—C5	−91.1 (5)	C6—C7—O7—C7′	174.7 (5)

Compound (4)

Crystal data

$C_{12}H_{13}Cl_3O$
$M_r = 279.59$
Orthorhombic
$P2_12_12_1$
$a = 9.818\,(2)$ Å
$b = 11.191\,(1)$ Å
$c = 11.790\,(1)$ Å
$V = 1295.4\,(3)$ Å^3
$Z = 4$
$D_x = 1.434$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 25 reflections
$\theta = 17$–$18°$
$\mu = 6.21$ mm^{-1}
$T = 292\,(2)$ K
Prismatic
0.310 × 0.308 × 0.256 mm
Colourless

Data collection

Rigaku AFC diffractometer
$w/2\theta$ scans
Absorption correction: Gaussian (*SHELX*76: Sheldrick, 1976)
$T_{\min} = 0.184$, $T_{\max} = 0.327$
1084 measured reflections
1084 independent reflections
1026 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 65.0°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 13$
3 standard reflections every 100 reflections intensity decay: <4.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 1.107$
$S = 1.109$
1084 reflections
159 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.0731P)^2 + 0.1681P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.017$
$\Delta\rho_{\max} = 0.190$ e Å^{-3}
$\Delta\rho_{\min} = -0.189$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.15 (5)

Table 2. *Selected geometric parameters (Å, °) for (4)*

C1—C2	1.562 (11)	C5—C6	1.503 (6)
C1—C7a	1.468 (8)	C5′—Cl5	1.701 (6)
C2—C3	1.495 (10)	C6—O6	1.380 (6)
C3—C3a	1.520 (7)	C6—C7	1.545 (7)
C3a—C4	1.576 (7)	C6—C8	1.592 (6)
C3a—C7a	1.525 (6)	O6—C6′	1.402 (7)
C3a—C8	1.538 (7)	C7—C7a	1.323 (8)
C4—C5	1.484 (7)	C8—Cl8	1.759 (4)
C5—C5′	1.354 (6)	C8—Cl8′	1.783 (4)
C2—C1—C7a	103.0 (4)	C5—C6—C8	99.3 (3)
C1—C2—C3	108.6 (7)	O6—C6—C7	118.8 (4)
C2—C3—C3a	105.8 (6)	O6—C6—C8	118.5 (4)
C3—C3a—C4	117.8 (5)	C7—C6—C8	98.1 (3)
C3—C3a—C7a	106.8 (4)	C6—O6—C6′	120.2 (5)
C3—C3a—C8	124.5 (5)	C6—C7—C7a	106.2 (4)
C4—C3a—C7a	105.0 (4)	C1—C7a—C7	140.5 (5)
C4—C3a—C8	101.3 (3)	C1—C7a—C3a	109.8 (5)
C7a—C3a—C8	98.5 (4)	C3a—C7a—C7	109.7 (4)
C3a—C4—C5	102.2 (4)	C3a—C8—C6	92.9 (3)
C4—C5—C5′	129.1 (5)	C3a—C8—Cl8	113.0 (3)
C4—C5—C6	107.4 (4)	C3a—C8—Cl8′	114.0 (3)
C5′—C5—C6	123.5 (4)	C6—C8—Cl8	116.5 (3)
C5—C5′—Cl5	121.3 (4)	C6—C8—Cl8′	112.4 (3)
C5—C6—O6	112.4 (4)	Cl8—C8—Cl8′	107.7 (2)
C5—C6—C7	107.1 (4)		
C1—C2—C3—C3a	17.8 (12)	C7a—C3a—C4—C5	67.5 (5)
C2—C3—C3a—C7a	−4.0 (9)	C3a—C4—C5—C5′	176.8 (5)
C3—C3a—C7a—C1	−12.2 (6)	C4—C5—C5′—Cl5	−1.0 (8)
C3a—C7a—C1—C2	22.2 (9)	C5′—C5—C6—O6	−16.0 (6)
C7a—C1—C2—C3	−24.8 (12)	C5—C6—O6—C6′	167.3 (5)
C3a—C4—C5—C6	−2.7 (5)	C2—C3—C3a—C8	109.3 (9)
C4—C5—C6—C7	−64.2 (5)	C7—C7a—C3a—C8	35.8 (5)
C5—C6—C7—C7a	67.9 (5)	C4—C5—C6—C8	37.3 (4)
C6—C7—C7a—C3a	0.1 (5)	C5—C6—C8—Cl8′	61.6 (4)
C7—C7a—C3a—C4	−68.4 (5)	C7a—C3a—C8—Cl8	68.0 (3)

Compound (2) crystallized as a racemic mixture and refinement was carried out on the 3a*S*,5*R*,6*R* enantiomer. However, the diagrams and torsion angles refer to the 3a*R*,5*S*,6*S* enantiomer, in accord with the chirality of other compounds in the series. Compound (4) crystallized as a racemic mixture and refinement was carried out on the 3a*S*,6*R* enantiomer. However, the diagrams and torsion angles refer to the 3a*R*,6*S* enantiomer, in accord with other related compounds in the series (see Mackay, Banwell & Phyland, 1977).

For both compounds, data collection: Rigaku AFC software; cell refinement: Rigaku AFC software; data reduction: Rigaku AFC software; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1168). Services for accessing these data are described at the back of the journal.

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