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A *gem*-Dichloro[4.3.1]propellane and a *gem*-Dichloro[5.3.1]propellenone

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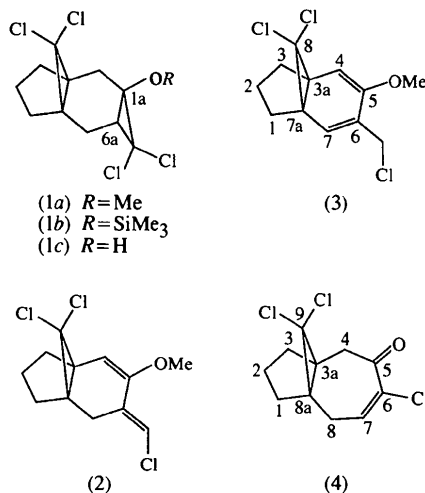
Abstract

X-ray analyses have established the structures of (3 α ,7 α)-6-chloromethyl-8,8-dichloro-2,3-dihydro-5-methoxy-3 α ,7 α -methano-1*H*-indene, C₁₂H₁₃Cl₃O, and (3 α ,8 α)-6,9,9-trichloro-2,3,5,8-tetrahydro-1*H*,4*H*-3 α ,8 α -methanoazulen-5-one, C₁₁H₁₁Cl₃O, which have resulted from different modes of cyclopropane ring cleavage within the framework of two closely related *gem*-dichloro[4.3.1]propellanes.

Comment

We have been developing new methods for the syntheses of *gem*-dihalogen[5.3.1]propellanes because of their utility in the construction of novel analogues of the anti-cancer agent TaxolTM (Banwell *et al.*, 1995). In this respect, we have studied the response of compounds (1*a*) and (1*b*) to various reaction conditions which might have been expected to effect the cleavage of the C1 α —C6 α bond, thereby providing the desired propellanes.

However, we have shown (Banwell *et al.*, 1994) that when compound (1*a*) is treated with a dilute solution of potassium *tert*-butoxide in tetrahydrofuran, C1 α —C6 α bond cleavage is observed and the major product of the reaction is compound (2). This ring-cleavage product was exceptionally unstable and, on standing, the compound rapidly converted into the double-bond isomer (3). In contrast, reaction of compound (1*b*) with silver acetate resulted in the formation of the desired type of ring-cleavage product, *viz.* the *gem*-dichloro-[5.3.1]propellenone (4), although this was accompanied by significant quantities of the alcohol (1*c*) (Banwell & Pallich, 1997). In view of the different modes of ring cleavage possible within the framework of (1), we have sought to characterize unequivocally the products of such processes in order to identify spectroscopic parameters which would allow ready structure identification. As part of this effort, we now present the results of the X-ray analyses of compounds (3) and (4).



The cyclopentane ring in each structure adopts a C2-envelope conformation with pseudo-rotation parameters (Altona *et al.*, 1968) Δ 37.6 and φ_m 9.0° for compound (3), and Δ 33.4 and φ_m 13.6° for compound (4). The cyclohexadiene ring atoms in (3) are coplanar to within 0.019 (2) Å (r.m.s. deviation 0.014 Å). The conformation of (4) is similar to the conformation of the propellanone system in a benzannulated [5.3.1]propellanone (Mackay *et al.*, 1997). The cycloheptene ring is a fairly regular boat, as indicated by the conformational asymmetry parameter (Duax & Norton, 1975) $\Delta C_s^{3a,8a}$ 9.6°. Atoms C4, C3 α , C8 α and C8 are coplanar (r.m.s. deviation 0.009 Å) to within 0.011 (3) Å, and atoms C4, C5, C6 and C7 are coplanar (r.m.s. deviation 0.04 Å) to within 0.04 (1) Å, with the interplanar angle being 122.7 (2)°. All bond lengths and angles are similar to those found in comparable structures.

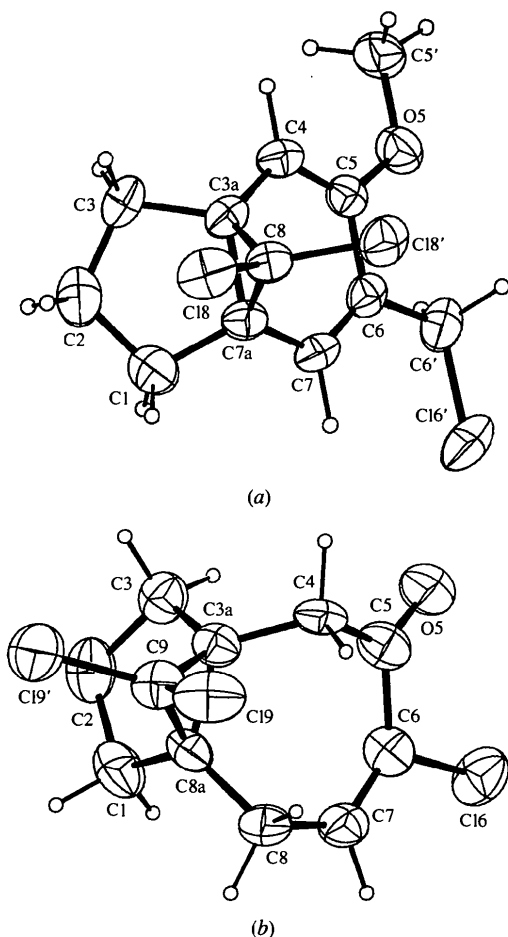


Fig. 1. Perspective views of the molecular structures of (a) the 3aS,7aR isomer of (3) and (b) 3aS,8aR isomer of (4), with displacement ellipsoids at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

Experimental

A tetrahydrofuran (THF) solution of (1a) (Banwell *et al.*, 1994) was added slowly to a stirred 0.05 M solution of potassium *tert*-butoxide in THF maintained at 273 K. The resulting mixture was stirred at 273 K for 1 h then subjected to a standard extractive work-up with ether. The light yellow solid thus obtained was subjected to chromatography (silica gel, hexane elution) and isolation of the appropriate fraction (R_f 0.3) gave (2) (Banwell *et al.*, 1994) as a colourless crystalline mass. On standing at 258 K for one week, this material rearranged to compound (3) which was recrystallized from acetone. A stirred mixture of compound (1b) and silver acetate (1.1 molar equivalents) in 4:1 glacial acetic acid-water was heated at reflux for 1 h. The cooled solution was subjected to standard extractive work-up with dichloromethane and the material so obtained was subjected to preparative thick-layer chromatography (silica gel, 1:9 ethyl acetate-hexane elution). Extraction of the chromatographically less mobile band (R_f 0.3) gave a solid, which upon recrystallization from ethanol afforded the alcohol (1c). Extraction of the

chromatographically more labile band (R_f 0.45) also gave a solid, which upon recrystallization from ethanol afforded crystals of compound (4).

Compound (3)

Crystal data

$C_{12}H_{13}Cl_3O$
 $M_r = 279.6$
 Monoclinic
 $P2_1/n$
 $a = 9.831$ (3) Å
 $b = 9.817$ (2) Å
 $c = 13.488$ (4) Å
 $\beta = 107.11$ (2)°
 $V = 1244.1$ (5) Å³
 $Z = 4$
 $D_x = 1.493$ Mg m⁻³
 $D_m = 1.48$ (1) Mg m⁻³
 D_m measured by flotation

Cu $K\alpha$ radiation
 $\lambda = 1.5418$ Å
 Cell parameters from 25 reflections
 $\theta = 16.5$ – 28.1 °
 $\mu = 6.47$ mm⁻¹
 $T = 292$ (2) K
 Prismatic
 0.145 (0.195) ×
 0.140 (0.192) ×
 0.042 (0.128) mm
 Colourless

Data collection

Rigaku AFC diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 Gaussian (SHELX76;
 Sheldrick, 1976)
 $T_{min} = 0.189$ (0.104),
 $T_{max} = 0.342$ (0.305)
 2236 measured reflections
 2053 independent reflections

1688 reflections with
 $I > 2\sigma(I)$
 $R_{int} = 0.049$
 $\theta_{max} = 65.1$ °
 $h = -11 \rightarrow 11$
 $k = 0 \rightarrow 11$
 $l = 0 \rightarrow 15$
 3 standard reflections
 every 100 reflections
 intensity decay: <12%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.145$
 $S = 1.152$
 2053 reflections
 158 parameters
 Only H-atom U 's refined
 $w = 1/[\sigma^2(F_o^2) + (0.0622P)^2 + 0.5971P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.008$
 $\Delta\rho_{max} = 0.284$ e Å⁻³
 $\Delta\rho_{min} = -0.378$ e Å⁻³
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected bond lengths (Å) for (3)

C1—C2	1.530 (6)	C5—C6	1.476 (4)
C1—C7a	1.512 (6)	O5'—C5'	1.444 (4)
C2—C3	1.534 (5)	C6—C6'	1.488 (4)
C3—C3a	1.527 (4)	C6—C7	1.346 (4)
C3a—C4	1.470 (4)	C6'—C16'	1.759 (4)
C3a—C7a	1.536 (4)	C7—C7a	1.470 (4)
C3a—C8	1.507 (4)	C7a—C8	1.514 (4)
C4—C5	1.340 (4)	C8—C18	1.762 (3)
C5—O5'	1.362 (4)	C8—C18'	1.760 (3)

Compound (4)

Crystal data

$C_{11}H_{11}Cl_3O$
 $M_r = 265.6$

Cu $K\alpha$ radiation
 $\lambda = 1.5418$ Å

Monoclinic

$P2_1/c$
 $a = 6.383$ (2) Å
 $b = 23.443$ (4) Å
 $c = 8.031$ (2) Å
 $\beta = 107.92$ (2)°
 $V = 1143$ (1) Å³
 $Z = 4$
 $D_x = 1.543$ Mg m⁻³
 D_m not measured

Data collection

Rigaku AFC diffractometer
 $\omega/2\theta$ scans
 Absorption correction:
 Gaussian (SHELX76;
 Sheldrick, 1976)
 $T_{\min} = 0.156$, $T_{\max} = 0.514$
 2084 measured reflections
 1928 independent reflections
 1173 reflections with
 $I > 2\sigma(I)$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.042$
 $wR(F^2) = 0.211$
 $S = 0.910$
 1928 reflections
 149 parameters
 Only H-atom U 's refined
 $w = 1/[\sigma^2(F_o^2) + (0.1473P)^2 + 0.136P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Cell parameters from 25

reflections
 $\theta = 18.8$ – 30.5°
 $\mu = 7.00$ mm⁻¹
 $T = 293$ (2) K
 Platelet
 $0.194 \times 0.192 \times 0.052$ mm
 Colourless

$R_{\text{int}} = 0.027$
 $\theta_{\text{max}} = 65.0^\circ$
 $h = -10 \rightarrow 10$
 $k = 0 \rightarrow 10$
 $l = 0 \rightarrow 14$
 3 standard reflections
 every 100 reflections
 intensity decay: <1.7%

$(\Delta/\sigma)_{\text{max}} = 0.014$
 $\Delta\rho_{\text{max}} = 0.446$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.413$ e Å⁻³
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)

Table 2. Selected bond lengths (Å) for (4)

C1—C8a	1.521 (7)	C5—C6	1.515 (6)
C1—C2	1.551 (5)	C6—C7	1.321 (4)
C2—C3	1.542 (8)	C6—C16	1.749 (5)
C3—C3a	1.507 (7)	C7—C8	1.525 (7)
C3a—C4	1.473 (7)	C8—C8a	1.520 (7)
C3a—C9	1.507 (6)	C8a—C9	1.518 (5)
C3a—C8a	1.540 (6)	C9—C19'	1.750 (3)
C4—C5	1.513 (7)	C9—C19	1.761 (4)
C5—O5	1.196 (4)		

As crystals of (3) were unstable in the X-ray beam, two crystals were used for the intensity measurements. The crystal dimensions and absorption corrections for the second crystal are given in parentheses in the experimental data.

For both compounds, data collection: *AFC/MSD Data Collection and Refinement Software* (Rigaku Corporation, 1974); cell refinement: *AFC/MSD Data Collection and Refinement Software*; data reduction: *AFC/MSD Data Collection and Refinement Software*; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELX76* (Sheldrick, 1976); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL93* (Sheldrick, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1196). Services for accessing these data are described at the back of the journal.

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Cyclohexanone-2,4,4,6-tetramethyl Ester†

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Abstract

The title compound, C₁₄H₁₈O₉, was isolated as a minor by-product (2.6%) from the benzene mother liquors of a preparation of Meerwein's ester. The molecule is present in the crystal in the enol configuration with the cyclohexene ring adopting a half-chair conformation.

Comment

In the course of a preparation of Meerwein's ester (Meerwein & Schurmann, 1913), the main compound was isolated in the published manner (Schaefer & Honig, 1968) from a benzene recrystallization. The mother liquors were left to stand for a few days and a highly crystalline second crop precipitated. As the ¹H NMR spectrum of the latter did not agree with that of the major compound, an X-ray analysis was undertaken to identify the minor product. A perspective view of the title compound, (I), is illustrated in Fig. 1.

† Alternative name: tetramethyl 2-hydroxycyclohexene-1,3,5,5-tetracarboxylate.