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(1*RS*,4*SR*)-3-Dichloromethylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene

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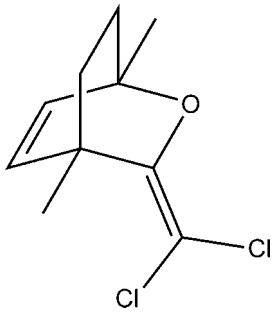
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.002 Å; R factor = 0.035; wR factor = 0.093; data-to-parameter ratio = 19.7.

X-ray crystallography was used to confirm the structure of the enantio-enriched title compound, $C_{10}H_{12}Cl_2O$, a bicylic enol ether. A bridged boat-like structure is adopted and the dichloromethylene C atom is positioned significantly removed from the core bicyclic unit. In the crystal structure, molecules pack to form sheets approximately perpendicular to the *a* and *c* axes.

Related literature

For related literature, see: Yamabe *et al.* (1996); Machiguchi *et al.* (1999); Khanjin *et al.* (1999); Ussing *et al.* (2006); Robertson & Fowler (2006).



Experimental

Crystal data

$C_{10}H_{12}Cl_2O$
M_r = 219.11
Monoclinic, $P2_1/c$
a = 9.3365 (1) Å
b = 9.6327 (2) Å
c = 11.4259 (2) Å
β = 92.7347 (11)°
V = 1026.43 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.59 mm^{-1}
T = 150 K
0.44 × 0.32 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.83, T_{max} = 0.90
4320 measured reflections
2321 independent reflections
2094 reflections with $I > 2\sigma(I)$
R_{int} = 0.021

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.093
S = 1.01
2321 reflections
118 parameters
2 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: Görbitz (1999) and *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2637).

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supplementary materials

Acta Cryst. (2008). E**64**, o1261 [**doi:10.1107/S1600536808017248**]

(1*RS*,4*SR*)-3-Dichloromethylene-1,4-dimethyl-2-oxabicyclo[2.2.2]oct-5-ene

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Comment

The reaction between dienes and ketenes to produce cyclobutanones was long considered to be a textbook example of a [2 + 2] cycloaddition that could be understood in terms of a $\pi 2_s + \pi 2_a$Woodward–Hoffmann formalism. More recently, evidence has been presented for a stepwise hetero-Diels–Alder/Claisen rearrangement pathway (Yamabe *et al.*, 1996) and it was reported that the periselectivity of these cycloadditions is responsive to the nature of the diene (Machiguchi *et al.*, 1999). The situation is, however, more complex and a combined theoretical and experimental study of the reaction of cyclopentadiene with either dichloro- or diphenylketene revealed that both [4 + 2] and [2 + 2] adducts may be produced directly through parallel reaction pathways traversing a bifurcating energy surface (Ussing *et al.* 2006). Our studies sought to address certain mechanistic aspects of the Claisen rearrangement of bicyclic enol ethers structurally analogous to those produced in diene/ketene [4 + 2] cycloadditions (Robertson & Fowler, 2006); within this study, although crystals were obtained as a racemate, the title compound was prepared in an enantioenriched form in order to determine if access to non-racemic cyclobutanones could be achieved.

The relationship between computed distances of reacting termini and activation energies has been discussed for structurally similar Claisen precursors in the context of the mechanism of chorismate mutase (Khanjin *et al.*, 1999). The molecular stucture (Fig. 1) shows the dichloromethylene carbon to be significantly removed from the carbon at C5 (3.5523 Å) and yet the title compound can be induced to undergo the Claisen rearrangement under mild thermal conditions to yield (1*RS*, 6*SR*)-8,8-dichloro-3,6-dimethylbicyclo[4.2.0]oct-3-en-7-one. Also of note are the sheets of molecules which form approximatedly perpendicular to the *a*- and *c*-axes as shown in Fig. 2 and Fig. 3.

Experimental

The title compound was crystallized by concentration of a sample dissolved in petroleum ether. $[\alpha]_D^{25}$-36.1 ($CHCl_3$, c = 1.0).

Refinement

Changes in illuminated volume were kept to a minimum, and were taken into account (Görbitz, 1999) by the multi-scan inter-frame scaling (*DENZO*/*SCALEPACK*, Otwinowski & Minor, 1997).

The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

Figures

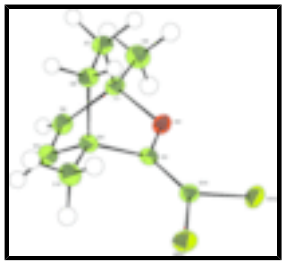

Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

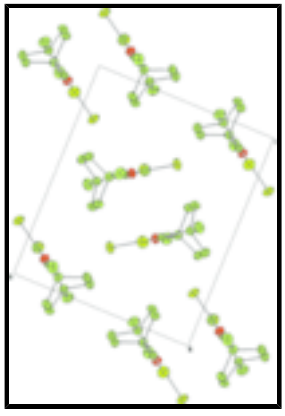

Fig. 2. The title compound viewed along the *a*-axis with H atoms omitted.

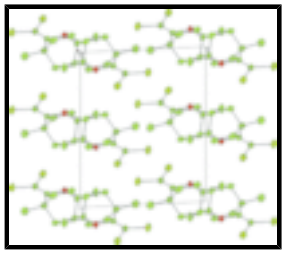

Fig. 3. The title compound viewed along the *b*-axis with H atoms omitted.

(1*RS*,4*SR*)-3-Dichloromethylene-1,4-dimethyl-2- oxabicyclo[2.2.2]oct-5-ene

Crystal data

$C_{10}H_{12}Cl_2O_1$	F_{000} = 456
M_r = 219.11	D_x = 1.418 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 15784 reflections
a = 9.3365 (1) Å	θ = 5–27º
b = 9.6327 (2) Å	μ = 0.59 mm^{-1}
c = 11.4259 (2) Å	T = 150 K
β = 92.7347 (11)º	Prism, colourless
V = 1026.43 (3) Å^3	0.44 × 0.32 × 0.18 mm
Z = 4	

Data collection

Nonius KappaCCD diffractometer	2094 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.021$
$T = 150$ K	$\theta_{max} = 27.4^{o}$
ω scans	$\theta_{min} = 5.1^{o}$
Absorption correction: multi-scan (DENZO/SCALEPACK; Otwinowski & Minor, 1997)	$h = -12 \rightarrow 12$
$T_{min} = 0.83$, $T_{max} = 0.90$	$k = -12 \rightarrow 12$
4320 measured reflections	$l = -14 \rightarrow 14$
2321 independent reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.034$	H-atom parameters constrained
$wR(F^2) = 0.093$	Method = Modified Sheldrick $w = 1/[\sigma^2(F^2) + (0.05P)^2 + 0.71P]$, where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.001$
2321 reflections	$\Delta\rho_{max} = 0.36$ e Å^{-3}
118 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
2 restraints	Extinction correction: None

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.02322 (16)	0.72676 (17)	0.56170 (14)	0.0234
O2	0.12271 (11)	0.62312 (12)	0.61475 (10)	0.0217
C3	0.26458 (15)	0.64956 (16)	0.59821 (13)	0.0192
C4	0.28716 (17)	0.77747 (17)	0.52291 (14)	0.0230
C5	0.21390 (19)	0.89526 (18)	0.58719 (15)	0.0293
C6	0.07027 (19)	0.86685 (17)	0.60962 (15)	0.0274
C7	0.04601 (18)	0.72396 (18)	0.43089 (14)	0.0280
C8	0.19575 (18)	0.75082 (18)	0.40893 (14)	0.0267
C9	−0.12456 (17)	0.6806 (2)	0.59357 (17)	0.0326
C10	0.44060 (19)	0.8143 (2)	0.49372 (17)	0.0339
C11	0.35800 (16)	0.56064 (17)	0.64983 (14)	0.0215
Cl12	0.29697 (4)	0.42007 (4)	0.72783 (4)	0.0295
Cl13	0.54194 (4)	0.56859 (5)	0.64989 (4)	0.0320
H51	0.2631	0.9775	0.6123	0.0403*
H61	0.0073	0.9265	0.6509	0.0362*

H71	−0.0214	0.7925	0.3907	0.0397*
H72	0.0158	0.6344	0.3998	0.0386*
H81	0.1990	0.8293	0.3587	0.0379*
H82	0.2347	0.6712	0.3675	0.0381*
H91	−0.1917	0.7492	0.5652	0.0477*
H92	−0.1261	0.6724	0.6804	0.0498*
H93	−0.1529	0.5941	0.5590	0.0483*
H101	0.4319	0.8976	0.4440	0.0529*
H102	0.5032	0.8374	0.5608	0.0543*
H103	0.4864	0.7409	0.4472	0.0531*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0213 (7)	0.0229 (7)	0.0254 (8)	0.0045 (6)	−0.0044 (6)	−0.0009 (6)
O2	0.0175 (5)	0.0225 (6)	0.0251 (5)	0.0016 (4)	0.0005 (4)	0.0041 (4)
C3	0.0188 (7)	0.0205 (7)	0.0183 (7)	−0.0023 (5)	0.0005 (5)	−0.0019 (6)
C4	0.0257 (7)	0.0220 (7)	0.0209 (7)	−0.0043 (6)	−0.0022 (5)	0.0018 (6)
C5	0.0373 (8)	0.0221 (8)	0.0275 (8)	0.0009 (7)	−0.0073 (7)	−0.0031 (7)
C6	0.0339 (8)	0.0229 (8)	0.0251 (8)	0.0055 (7)	−0.0030 (6)	−0.0032 (6)
C7	0.0347 (8)	0.0264 (8)	0.0223 (8)	0.0014 (7)	−0.0067 (6)	−0.0013 (6)
C8	0.0352 (8)	0.0268 (8)	0.0178 (7)	−0.0025 (7)	−0.0026 (6)	0.0010 (6)
C9	0.0212 (8)	0.0328 (9)	0.0435 (10)	0.0028 (7)	−0.0005 (7)	−0.0031 (8)
C10	0.0309 (9)	0.0345 (10)	0.0360 (9)	−0.0126 (7)	−0.0013 (7)	0.0072 (8)
C11	0.0189 (7)	0.0234 (7)	0.0222 (7)	−0.0011 (6)	0.0001 (5)	0.0004 (6)
Cl12	0.0292 (2)	0.0261 (2)	0.0329 (2)	−0.00012 (15)	−0.00257 (16)	0.01006 (16)
Cl13	0.0183 (2)	0.0372 (3)	0.0401 (3)	0.00107 (15)	−0.00273 (16)	0.00256 (18)

Geometric parameters (Å, °)

C1—O2	1.4741 (18)	C7—C8	1.455 (2)
C1—C6	1.514 (2)	C7—H71	1.008
C1—C7	1.520 (2)	C7—H72	0.970
C1—C9	1.511 (2)	C8—H81	0.950
O2—C3	1.3707 (17)	C8—H82	0.980
C3—C4	1.523 (2)	C9—H91	0.957
C3—C11	1.339 (2)	C9—H92	0.996
C4—C5	1.531 (2)	C9—H93	0.954
C4—C8	1.544 (2)	C10—H101	0.985
C4—C10	1.528 (2)	C10—H102	0.968
C5—C6	1.404 (3)	C10—H103	0.993
C5—H51	0.953	C11—Cl12	1.7324 (16)
C6—H61	0.962	C11—Cl13	1.7190 (15)
O2—C1—C6	106.78 (12)	C1—C7—H72	108.9
O2—C1—C7	106.10 (12)	C8—C7—H72	111.1
C6—C1—C7	108.65 (14)	H71—C7—H72	104.6
O2—C1—C9	105.44 (13)	C4—C8—C7	112.39 (13)
C6—C1—C9	115.34 (14)	C4—C8—H81	110.2

C7—C1—C9	113.84 (14)	C7—C8—H81	107.7
C1—O2—C3	114.30 (12)	C4—C8—H82	109.5
O2—C3—C4	112.89 (12)	C7—C8—H82	109.0
O2—C3—C11	115.71 (13)	H81—C8—H82	107.9
C4—C3—C11	131.40 (14)	C1—C9—H91	107.8
C3—C4—C5	104.57 (13)	C1—C9—H92	108.7
C3—C4—C8	104.84 (12)	H91—C9—H92	110.5
C5—C4—C8	106.63 (13)	C1—C9—H93	113.3
C3—C4—C10	117.88 (14)	H91—C9—H93	107.4
C5—C4—C10	112.19 (14)	H92—C9—H93	109.1
C8—C4—C10	109.92 (13)	C4—C10—H101	105.3
C4—C5—C6	113.31 (14)	C4—C10—H102	114.7
C4—C5—H51	122.7	H101—C10—H102	107.4
C6—C5—H51	123.9	C4—C10—H103	112.5
C1—C6—C5	111.77 (14)	H101—C10—H103	107.3
C1—C6—H61	122.4	H102—C10—H103	109.2
C5—C6—H61	125.8	C3—C11—Cl12	120.21 (12)
C1—C7—C8	110.31 (13)	C3—C11—Cl13	126.97 (12)
C1—C7—H71	108.8	Cl12—C11—Cl13	112.82 (9)
C8—C7—H71	112.9		

Fig. 1

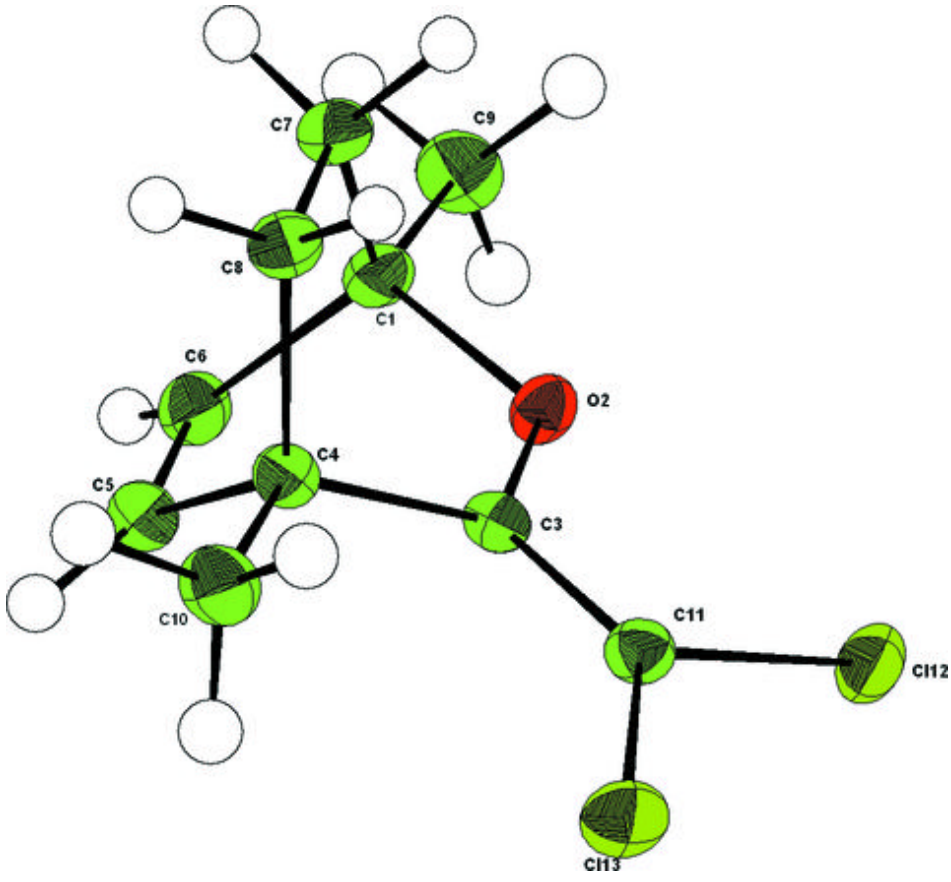

Fig. 2

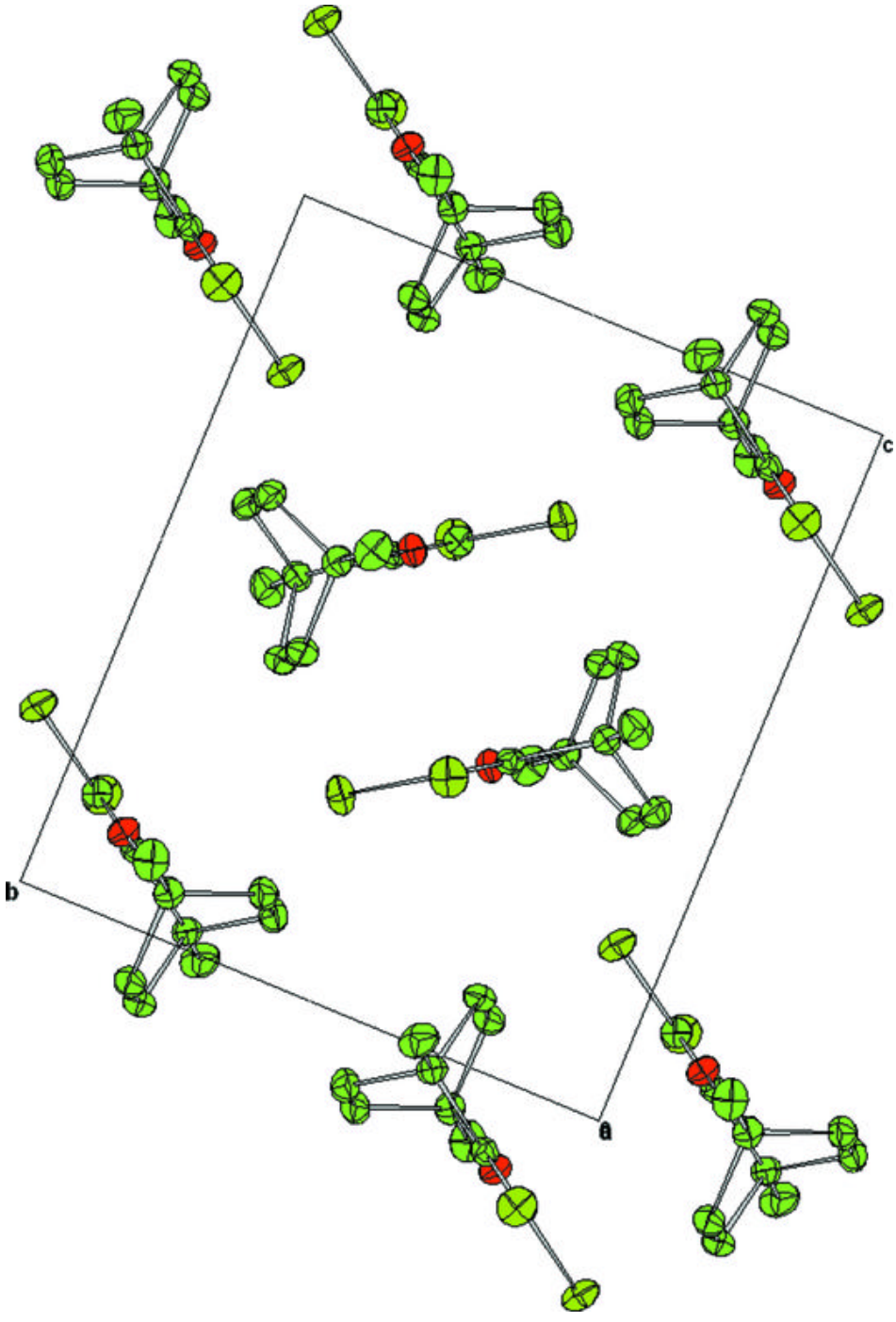

Fig. 3