organic papers

exo-(1RS,8SR,9RS,11SR)-10-Chloromethyl-tetracyclo[6.3.2.0²,⁷0⁹,¹¹]undecane-2,4,6,12-tetraene

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The title compound, $C_{14}H_{13}Cl$, consists of two central non-planar six-membered carbon rings constituting a bicyclic system, having a benzene ring fused on one side and a >CHCH$_2$Cl moiety, bridging the two C atoms of the bicyclic system, thereby forming a fused three-atom ring on the other side. The bicyclic system has approximate D_3 symmetry and all three six-membered rings adopt boat conformations.
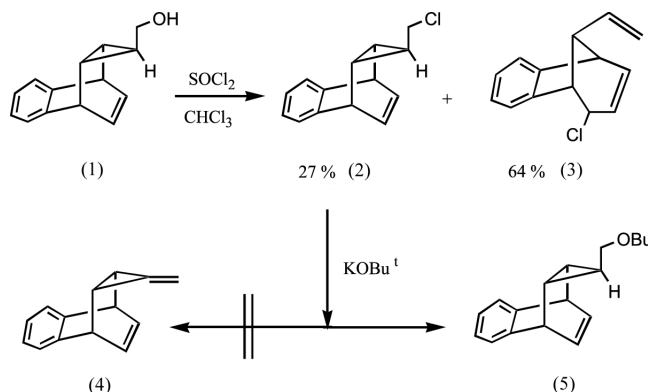
Comment

In general, organohalogen compounds are used extensively as solvents and insecticides, and as starting materials for the synthesis of other organic compunds. Treatment of alkyl halides with a strong base such as KO^{t}Bu gives the corresponding alkenes (Fessenden & Fessenden, 1993).

As shown in the scheme, chloride (2) was isolated from the reaction of alcohol (1) with thionyl chloride and reacted with KO^{t}Bu to yield compound (5), a substituted product, instead of alkene (4) (Menzek, 2000). A similar reaction has been reported in the literature (Stampfli & Nuenschwander, 1988). For the formation of the product with O^{t}Bu, the structure of chloride (2) is important.

The structures of [3.2.1]- and [2.2.2]-bicyclic systems having different substituents at different positions of the bicyclic framework have been the subject of much interest in our laboratory; examples are exo,endo,endo-9,9,10,11,12-penta-bromotricyclo[6.2.2.0²,⁷]dodeca-2(7),3,5-triene [(II); Hökelek et al., 1990], exo,,exo-9,10,12-tribromotricyclo[6.3.1.0²,⁷]-dodeca-2(7),3,5,10-tetraene [(III); Hökelek et al., 1991], exo,exo-2,4,8-tribromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene, (IV), endo,exo-2,3,8-tribromo-6,7-benzobicyclo[3.2.1]octa-3,6-diene, (V), and exo,endo-2,5,6-tribromo-6,7-benzotricyclo[2.2.2]octa-2,6-diene, (VI) (Balcı et al., 1992), exo,anti-4-hydroxy-8-bromo-6,7-benzobicyclo[3.2.1]octa-2,6-diene, (VII), exo,anti-4,8-dibromo-2,3-benzobicyclo[3.2.1]octa-2,6-
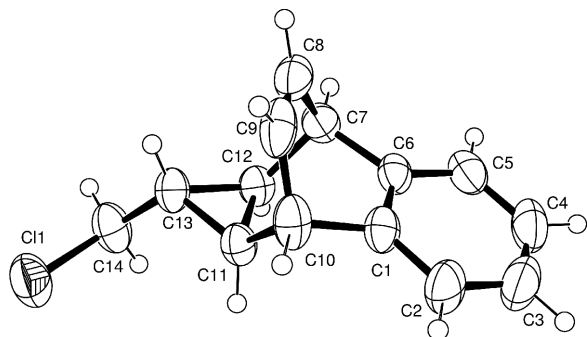
Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

diene, (VIII), and *endo,endo*-7,8-dibromo-5,6-benzobicyclo[2.2.2]octa-2,5-ene, (IX) (Daştan *et al.*, 1994), *exo,exo*-2,3-*endo,endo*-5,6-tetrabromobicycloheptane [(X); Hökelek *et al.*, 1998], and 2,2-*exo*-3,5,6-pentabromobicycloheptane [(XI); Hökelek *et al.*, 2001].

The structure determination of the title compound, (2), was undertaken in order to verify the formation of the chloride.

The title compound, (2), contains two central non-planar six-membered carbon rings constituting a bicyclic system, which has a benzene (C1–C6) ring (*A*) on one side and a >CHCH$_2$Cl moiety, bridging the two C atoms of the bicyclic system, thereby forming a fused three-membered ring on the other side (Fig. 1). As can be seen from the torsion angles (Table 1) and the puckering parameters (Cremer & Pople, 1975), the bicyclic system has approximate D_3 symmetry.

In the bicyclic fragment, all three six-membered rings adopt boat conformations: $Q_T = 0.776\,(21)$ Å, $\varphi_2 = -179.95\,(15)°$ and $\theta_2 = 90.47\,(15)°$ for the C7–C12 ring, $Q_T = 0.772\,(2)$ Å, $\varphi_2 = 119.14\,(14)°$ and $\theta_2 = 89.64\,(12)°$ for the C1/C6–C10 ring, and $Q_T = 0.889\,(2)$ Å, $\varphi_2 = -59.69\,(13)°$ and $\theta_2 = 89.25\,(13)°$ for the C1/C6/C7/C12/C11/C10 ring.

Slight bond alternation is observed in ring *A*, with the distal aromatic bond C3—C4 [1.363 (3) Å] being about 0.03 Å shorter than the proximal bond C1—C6 [1.394 (2) Å].

Bond angles about the central bicyclic system deviate substantially from ideal values. The exterior angles C2—C1—C10 [126.9 (2)°] and C5—C6—C7 [127.3 (2)°] [average 127.1 (2)°] are larger than the interior angles C13—C11—C10 [122.5 (2)°] and C13—C12—C7 [123.5 (2)°] [average 123.0 (2)°]. The tetrahedral angles also exhibit significant distortion: C6—C7—C12 [103.5 (2)°] and C1—C10—C11 [102.9 (2)°] [average 103.2 (2)°], and C6—C7—C8 [106.6 (2)°], C12—C7—C8 [108.4 (2)°], C1—C10—C9 [106.9 (2)°] and C11—C10—C9 [109.2 (2)°] [average 107.8 (2)°]. The average values of the corresponding exterior and tetrahedral angles in similar [2.2.2]-bicyclic systems are 126.1 (5), 107.1 (4) and 107.9 (4)° in (II), 126.6 (9), 108.5 (7) and 105.6 (7)° in (VI), and 126.5 (6), 107.1 (5) and 106.5 (6)° in (IX), respectively. The angles C7—C8—C9 [114.3 (2)°] and C10—C9—C8 [114.8 (2)°] about the double bond have an average value of 114.5 (2)°. These results indicate the presence of significant
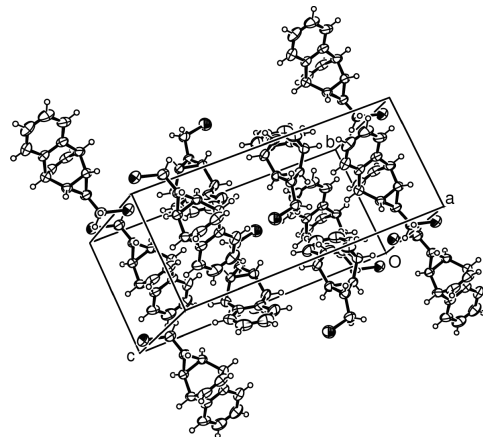

Figure 2
Packing diagram of (2).

strain in the bicyclic framework. The degree of strain is manifest most obviously in the deviations from ideality of the bond angles in the bicyclic ring system. However, the strain in the [3.2.1]-bicyclic system is more predominant than in the bicyclo[2.2.2]octane skeleton (Hökelek *et al.*, 1991).

The dihedral angles between planes *A*, *B* (C1/C6/C7/C10), *C* (C7–C10), *D* (C7/C10–C12) and *E* (C11–C13) are as follows: $A/B = 1.73\,(7)°$, $B/C = 57.79\,(8)°$, $B/D = 65.22\,(9)°$, $C/D = 56.99\,(10)°$ and $D/E = 62.71\,(11)°$.

As can be seen from the packing diagram (Fig. 2), the molecules are elongated approximately parallel to the *b* axis and stacked along the *a* axis. Dipole–dipole and van der Waals interactions are effective in the molecular packing.

Experimental

Crystal data

C$_{14}$H$_{13}$Cl	$D_x = 1.278$ Mg m^{-3}
$M_r = 216.69$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2865
$a = 8.0400\,(8)$ Å	reflections
$b = 7.8514\,(7)$ Å	$\theta = 2.3–28.0°$
$c = 18.1877\,(16)$ Å	$\mu = 0.30$ mm^{-1}
$\beta = 101.133\,(2)°$	$T = 293\,(2)$ K
$V = 1126.50\,(18)$ Å^3	Irregular, colourless
$Z = 4$	$0.30 \times 0.25 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.037$
φ and ω scans	$\theta_{max} = 28.0°$
Absorption correction: none	$h = -8 \rightarrow 10$
6442 measured reflections	$k = -10 \rightarrow 10$
2590 independent reflections	$l = -23 \rightarrow 19$
1441 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R[F^2 > 2\sigma(F^2)] = 0.042$	independent and constrained
$wR(F^2) = 0.098$	refinement
$S = 0.85$	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2]$
2590 reflections	where $P = (F_o^2 + 2F_c^2)/3$
172 parameters	$(\Delta/\sigma)_{max} < 0.001$
	$\Delta\rho_{max} = 0.14$ e Å^{-3}
	$\Delta\rho_{min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cl1—C14	1.7935 (19)	C1—C2	1.373 (3)
C12—C11	1.493 (2)	C1—C10	1.519 (3)
C12—C13	1.509 (2)	C13—C14	1.495 (2)
C12—C7	1.552 (2)	C7—C8	1.503 (3)
C6—C5	1.379 (2)	C5—C4	1.386 (3)
C6—C1	1.394 (2)	C10—C9	1.503 (3)
C6—C7	1.518 (2)	C9—C8	1.317 (3)
C11—C13	1.499 (2)	C2—C3	1.391 (3)
C11—C10	1.549 (2)	C3—C4	1.363 (3)
C11—C12—C13	59.91 (11)	C14—C13—C12	116.79 (17)
C11—C12—C7	110.67 (15)	C11—C13—C12	59.49 (11)
C13—C12—C7	123.51 (16)	C8—C7—C6	106.56 (16)
C5—C6—C7	127.33 (18)	C8—C7—C12	108.37 (15)
C1—C6—C7	112.87 (15)	C6—C7—C12	103.53 (15)
C12—C11—C13	60.60 (11)	C9—C10—C1	106.91 (16)
C12—C11—C10	109.79 (16)	C9—C10—C11	109.16 (17)
C13—C11—C10	122.51 (18)	C1—C10—C11	102.92 (15)
C2—C1—C10	126.94 (19)	C13—C14—Cl1	112.06 (13)
C6—C1—C10	112.46 (16)	C8—C9—C10	114.79 (19)
C14—C13—C11	117.98 (18)	C9—C8—C7	114.3 (2)
C7—C12—C11—C10	0.7 (2)	C12—C11—C10—C9	53.0 (2)
C7—C6—C1—C10	−1.6 (2)	C12—C11—C10—C1	−60.3 (2)
C1—C6—C7—C8	54.7 (2)	C1—C10—C9—C8	54.8 (2)
C1—C6—C7—C12	−59.52 (18)	C11—C10—C9—C8	−55.8 (2)
C11—C12—C7—C8	−54.3 (2)	C10—C9—C8—C7	−0.7 (2)
C11—C12—C7—C6	58.57 (18)	C6—C7—C8—C9	−54.3 (2)
C6—C1—C10—C9	−52.3 (2)	C12—C7—C8—C9	56.6 (2)
C6—C1—C10—C11	62.7 (2)		

Most of the H atoms were located in a difference synthesis and refined isotropically [C—H = 0.94 (2)–0.99 (2) Å]. Atoms H3, H4, H14A and H14B were positioned geometrically at distances of 0.93 (CH) and 0.97 Å (CH$_2$) from the parent C atoms; a riding model was used for these during the refinement process. The U_{iso} values were constrained to be 1.2 times U_{eq} of the carrier atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999) and *SHELXTL* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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