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2,2-*exo*-3,5,6-Pentabromobicycloheptane

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.016 Å
R factor = 0.064
wR factor = 0.133
Data-to-parameter ratio = 19.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The title compound, $C_7H_7Br_5$, consists of a norbornane skeleton composed of two five-membered rings in envelope conformations or a six-membered ring with five Br atoms held in a boat conformation by a bridging methylene group. The repulsive interactions between the Br atoms affect the topology of the norbornane moieties.

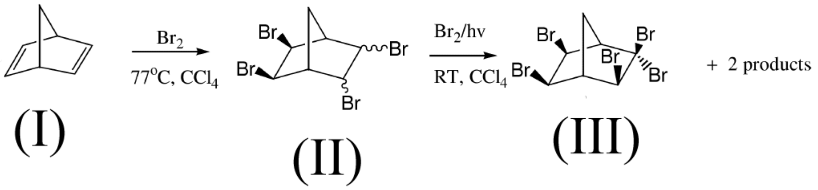
Comment

The constitution and configuration of the products formed by electrophilic addition to norbornane and norbornadienes are interesting (Traylor, 1969). The reactions of these systems have been used as mechanistic probes to elucidate the mechanism of different reactions. Bromonorbornanes are important in the synthesis of bromonorbornadienes which may be used for other substituted norbornadienes.

Halogenation of norbornadiene has been studied less extensively (Alvernhe *et al.*, 1988; Gregorcic & Zupabn, 1977). Winstein has studied bromination of norbornadiene and has pointed out dangerous properties of the products (Winstein, 1961).

In the course of studying the bromination reactions of unsaturated bicyclic systems, we noticed that the reaction temperature has a dramatic influence on product distribution (Balcı *et al.*, 1992*a*,*b*). In connection with our continuing work in the bromination reactions, we carried out brominations in photolytic and high-temperature conditions to prevent the skeletal rearrangement, *i.e.* to obtain normal addition products.

Addition of bromine to norbornadiene results in the products of Wagner–Meerwein rearrangement and homoallylic conjugation. Recently, we succeeded in obtaining the normal addition product, *i.e.* 2,3,5,6-tetrabromonorbornanes (II), and developed a synthetic methodology leading to dibromonorbornadiene by dehydrobromination of (II) (Tutar *et al.*, 1996). We are now interested in photobromination of tetrabromonorbornanes (II) to obtain further brominated norbornanes and other norbornane derivatives.



Bromination of norbornadiene at reflux temperature of the solvent (CCl_4) yields three diastereomeric 2,3,5,6-tetrabromonorbornanes [TBN, (II)] and two 3,5-dibromo-

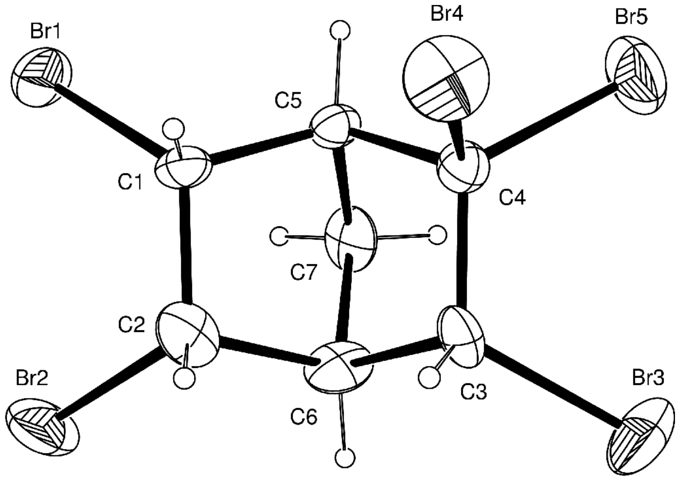


Figure 1
An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

nortricyclanes [DBN, (III)] which are easily isolated by simple distillation in two parts in a yield of 40 and 54%, respectively (Tutar *et al.*, 1996). In an initial experiment, photobromination of (II) was carried out at room temperature. After crystallization and combined silica-gel column chromatography eluting with hexane, we isolated three compounds. Because of the very close similarity, we were not able to make a clear-cut differentiation between the stereochemistries in any of these materials containing five Br atoms. Therefore, we carried out the structure determination of compound (III).

The molecule (Fig. 1) contains the norbornane skeleton, composed of two fused five-membered rings in envelope conformation or of a six-membered ring held in a boat conformation by a bridging methylene group. There is an approximately tetrahedral environment about the C4 atom, but the Br4—C4—Br5 [105.4 (5)°] angle is smaller and Br5—C4—C3 [116.6 (7)°] angle is larger than the conventional value of the tetrahedral angle. The C4—C3—Br3 [117.9 (7)°] angle is also larger than the other angles about C3. This behavior appears to be a result of a repulsive interaction between atoms Br3 and Br5. Similarly, the Br1—C1—C2 [117.4 (7)°] and Br2—C2—C1 [117.3 (8)°] angles are larger than the other angles about C1 and C2, respectively, probably because of the repulsion between atoms Br1 and Br2. The Br—C bond lengths are nearly equal and average 1.95 (1) Å. The C—C single bond lengths range from 1.50 (1) to 1.58 (2) Å, with a mean value of 1.54 (2) Å.

The topology of the norbornane moieties in the title compound, (III), is consistent with that reported in other norbornanes. The value of the C5—C7—C6 [95.9 (9)°] angle is markedly different from the tetrahedral value. In other norbornane derivatives, the corresponding angle is reported as 93.3 (8)° in *exo,exo*-2,3-*endo,endo*-5,6-tetrabromobicycloheptane (Hökelek *et al.*, 1998), 94.3 (7)° in 2,2-*exo*-3,5,5-*exo*-6-hexabromobicycloheptane (Akkurt *et al.*, 2000) and 101.0 (9)° in *endo,exo*-9,11-dibromotricyclo-[6.3.1.0^{2,7}]dodeca-2 (7),3,5-triene-10-one (Büyükgüngör, 1989).

The Br—C—C bond angles are between 106.8 (7) and 117.9 (7)°, with an average value of 112.6 (7)°, which is 111.2 (3)° in *exo,endo,endo*-9,9,10,11,12-pentabromotricyclo[6.2.2.0^{2,7}]dodeca-2 (7),3,5- triene (Hökelek *et al.*, 1990), 115.1 (6)° in *exo,exo*-9,10,12-tribromotricyclo[6.3.1.0^{2,7}]-dodeca-2(7),3,5,10-tetraene (Hökelek *et al.*, 1991) and 113.9 (7)° in *exo,exo*-2,3-*endo,endo*-5,6-tetrabromobicycloheptane (Hökelek *et al.*, 1998).

The deviations of the Br1, Br2, Br3, Br4 and Br5 atoms from the least-squares plane passing through the C1/C2/C3/C4 atoms are 0.827 (1), 0.781 (1), 0.603 (2), −1.828 (1) and 0.883 (1) Å, respectively. An examination of the deviations from the least-squares planes through the individual fragments shows that the fragments *A*(C5—C1—C2—C6) and *B*(C5—C4—C3—C6) are nearly planar. The dihedral angles between *A*, *B* and *C*(C5,C6,C7) are *A*/*B* = 68.3 (5), *A*/*C* = 56.1 (7) and *B*/*C* = 55.7 (6)°.

The strain in the structures containing one atom in the bridge is more predominant than in structures containing two C atoms in the bridge (Hökelek *et al.*, 1990).

Experimental

A solution of excess Br_2 (4 equivalents) was added to a solution of tetrabromonorbornadiene (4.12 g, 10.0 mmol) in CCl_4 (40 ml), in an internal-type photochemical reaction apparatus. The reaction mixture was irradiated with a projector lamp (350 W) and the reaction progress was monitored by NMR. The resulting mixture was crystallized from methylene chloride–hexane and chromatographed with silica gel, eluting with hexane. Compound (III) was isolated in a yield of 4% (196 mg). It was recrystallized from a methylene chloride–petroleum ether mixture over a period of 12 h (m.p. 403 K).

Crystal data

$C_7H_7Br_5$
$M_r = 490.63$
Monoclinic, $P2_1/c$
$a = 6.765$ (2) Å
$b = 13.822$ (2) Å
$c = 12.114$ (3) Å
$\beta = 94.92$ (2)°
$V = 1128.6$ (5) Å^3
$Z = 4$

$D_x = 2.888$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10$–18°
$\mu = 17.75$ mm^{-1}
$T = 294$ (2) K
Rod, colorless
0.30 × 0.10 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (*MolEN*; Fair, 1990)
$T_{\min} = 0.137$, $T_{\max} = 0.169$
2599 measured reflections
2291 independent reflections
1112 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.015$
$\theta_{\max} = 26.3°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 17$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.133$
$S = 0.98$
2201 reflections
111 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0557P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.04$ e Å^{-3}
$\Delta\rho_{\min} = -0.91$ e Å^{-3}

o710 Tuncer Hökelek *et al.* • $C_7H_7Br_5$ *Acta Cryst.* (2001). E**57**, o709–o711

Table 1
Selected geometric parameters (Å, °).

Br1—C1	1.947 (11)	Br4—C4	1.959 (11)
Br2—C2	1.971 (11)	Br5—C4	1.948 (10)
Br3—C3	1.937 (11)		
C2—C1—Br1	117.4 (7)	Br3—C3—H31	108.2
C5—C1—Br1	107.8 (7)	C3—C4—Br5	116.6 (7)
C1—C2—Br2	117.3 (8)	C5—C4—Br5	106.8 (7)
C6—C2—Br2	107.7 (8)	C3—C4—Br4	110.3 (7)
Br2—C2—H21	109.2	C5—C4—Br4	113.8 (7)
C4—C3—Br3	117.9 (7)	Br5—C4—Br4	105.4 (5)
C6—C3—Br3	110.7 (8)	C5—C7—C6	95.5 (9)
Br1—C1—C2—Br2	−3.0 (12)	Br3—C3—C4—Br4	−111.1 (8)
Br3—C3—C4—Br5	9.0 (12)	C1—C5—C7—C6	−56.4 (10)

The positions of the H atoms were calculated geometrically at distances of 0.98 (CH) and 0.97 Å (CH_2) from the carrier atoms, and a riding model was used during the refinement process.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *MolEN*.

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Acta Cryst. (2001). E**57**, o709–o711 Tuncer Hökelek *et al.* • $C_7H_7Br_5$ **o711**