

plane of the aromatic ring by the presence of nitro substituents on each side, which facilitates the replacement of methoxy by an amino group.

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Structures and Absolute Configurations of (–)-6-endo-9-Dibromocamphor and (–)-7-anti-9-Dibromofenchone*

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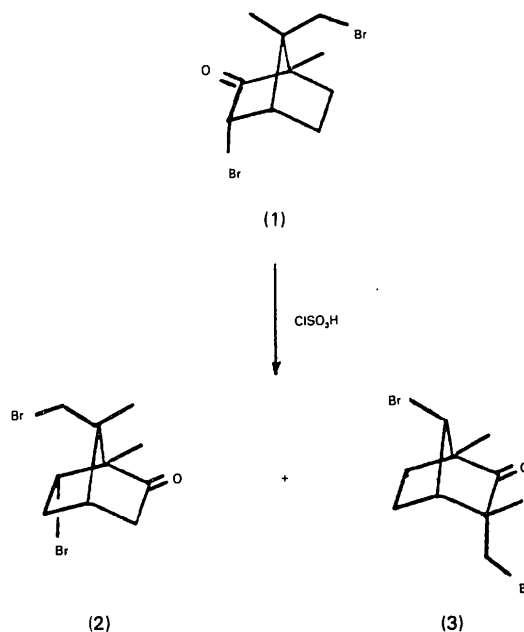
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Abstract. $C_{10}H_{14}Br_2O$, $M_r = 310.03$, $Mo K\alpha$, $\lambda_{\alpha_1} = 0.70930 \text{ \AA}$, $T = 295 \text{ K}$; dibromocamphor, monoclinic, $P2_1$, $a = 7.583 (1)$, $b = 11.081 (1)$, $c = 6.739 (1) \text{ \AA}$, $\beta = 101.457 (4)^\circ$, $V = 554.98 (9) \text{ \AA}^3$, $Z = 2$, $D_x = 1.855 (1) \text{ g cm}^{-3}$, $\mu = 72 \text{ cm}^{-1}$, $F(000) = 304$, $R = 0.054$ for 925 reflections; dibromofenchone, orthorhombic, $P2_12_12_1$, $a = 7.022 (1)$, $b = 12.467 (1)$, $c = 13.302 (1) \text{ \AA}$, $V = 1164.5 (2) \text{ \AA}^3$, $Z = 4$, $D_x = 1.768 (1) \text{ g cm}^{-3}$, $\mu = 69 \text{ cm}^{-1}$, $F(000) = 608$, $R = 0.037$ for 691 reflections. The structures and absolute configurations of the two rearrangement products of (+)-3-endo-9-dibromocamphor have been established. The molecular geometries and dimensions are similar to those of related materials: mean C–Br lengths are $1.97 (1) \text{ \AA}$, C(1)–C(7)–C(4) bridgehead angles $95.3 (8)$ and $95.7 (8)^\circ$.

Introduction. Treatment of (+)-3-endo-9-dibromocamphor (1) with chlorosulfonic acid leads to a remarkable rearrangement with inversion of configuration, producing (–)-6-endo-9-dibromocamphor (2) and (–)-7-anti-9-dibromofenchone (3) (Money, 1985; Antoniadis, Hutchinson & Money, 1987). Since it was

important to establish the stereochemical course of the reaction unambiguously, the present analysis was designed to determine the structures and absolute configurations of the products.



* (1*S*,4*R*,6*S*,7*S*)-6-Bromo-7-bromomethyl-1,7-dimethyl- and (1*R*,3*R*,4*S*,7*S*)-7-bromo-3-bromomethyl-1,3-dimethylbicyclo[2.2.1]heptan-2-one.

Table 1. Final positional (fractional $\times 10^4$) and isotropic thermal parameters ($\times 10^3 \text{ \AA}^2$) with estimated standard deviations in parentheses

$U_{eq} = \frac{1}{3}$ trace of the diagonalized U tensor.

	x	y	z	U_{eq}
6-endo-9-Dibromocamphor				
Br(1)	11646 (2)	1771	2843 (2)	55
Br(2)	3960 (2)	3499 (2)	-2193 (2)	58
O	9407 (11)	3223 (10)	6177 (11)	57
C(1)	8732 (11)	3526 (12)	2513 (13)	32
C(2)	8554 (13)	2944 (11)	4537 (16)	41
C(3)	7079 (15)	2014 (12)	4127 (17)	46
C(4)	6405 (13)	2161 (10)	1784 (17)	31
C(5)	7874 (14)	1592 (10)	799 (17)	39
C(6)	9418 (14)	2507 (10)	1316 (15)	33
C(7)	6671 (12)	3518 (11)	1489 (12)	30
C(8)	5537 (15)	4350 (12)	2581 (16)	40
C(9)	6384 (14)	3908 (10)	-714 (16)	41
C(10)	9804 (18)	4694 (12)	2645 (19)	53

	x	y	z	U_{eq}
7-anti-9-Dibromofenchone				
Br(1)	2174.1 (2.7)	6627.4 (1.1)	621.3 (1.3)	91
Br(2)	1912.6 (2.4)	2112.3 (1.2)	2659.1 (1.1)	85
O	6969 (12)	3458 (7)	535 (7)	71
C(1)	4654 (18)	4822 (9)	169 (9)	51
C(2)	5532 (16)	3918 (10)	772 (9)	48
C(3)	4331 (18)	3694 (8)	1685 (9)	47
C(4)	2629 (19)	4470 (8)	1468 (8)	52
C(5)	1511 (16)	4088 (11)	561 (11)	66
C(6)	2905 (21)	4272 (10)	-319 (8)	59
C(7)	3776 (19)	5432 (8)	1051 (9)	52
C(8)	5959 (21)	5395 (11)	-567 (12)	79
C(9)	3855 (19)	2498 (9)	1664 (9)	54
C(10)	5405 (25)	3965 (13)	2646 (10)	86

Experimental. Colourless crystals, dimensions $0.2 \times 0.2 \times 0.5$ mm for the camphor derivative (2) [$0.9 \times 0.5 \times 0.28$ mm for the fenchone derivative (3)], crystal faces $\{010\}$, $\pm(1\bar{1}0)$, $\pm(2\bar{1}0)$, and smaller end faces $\{(100), (\bar{1}0\bar{1}), \{011\}\}$, Enraf-Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 15\text{--}21^\circ$ [$15\text{--}17^\circ$]. Intensities for $\theta \leq 27.5^\circ$ [25°], hkl : -9 to 9 , 0 to 14 , 0 to 8 [0 to 8 , 0 to 14 , 0 to 15], ω - 2θ scan, ω scan width $(0.75 + 0.35 \tan \theta)^\circ$ at $1.1\text{--}10^\circ \text{ min}^{-1}$, extended 25% on each side for background measurement, three standard reflections (average 2% decay [no decay]), Lp and absorption corrections, transmission factors $0.22\text{--}0.39$ [$0.050\text{--}0.163$], 1336 [1207] unique reflections measured, 925 [691] with $I \geq 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0.04I)^2$, S = scan, B_1 and B_2 = background counts. Structure by Patterson and Fourier methods, refined by full-matrix least squares on F , H fixed in calculated positions, $w = 1/\sigma^2(F)$, scattering factors from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs, final $R = 0.054$, $wR = 0.054$ for

Table 2. Bond lengths (\AA) and angles ($^\circ$) with estimated standard deviations in parentheses

6-endo-9-Dibromocamphor		7-anti-9-Dibromofenchone	
Br(1)–C(6)	1.971 (11)	Br(1)–C(7)	1.953 (12) 1.960
Br(2)–C(9)	1.962 (11)	Br(2)–C(9)	1.960 (12) 1.970
O–C(2)	1.205 (13)	O–C(2)	1.203 (13) 1.208
C(1)–C(2)	1.538 (14)	C(1)–C(2)	1.51 (2) 1.52
C(1)–C(6)	1.54 (2)	C(1)–C(6)	1.55 (2) 1.56
C(1)–C(7)	1.579 (12)	C(1)–C(7)	1.53 (2) 1.54
C(1)–C(10)	1.52 (2)	C(1)–C(8)	1.52 (2) 1.53
C(2)–C(3)	1.51 (2)	C(2)–C(3)	1.50 (2) 1.52
C(3)–C(4)	1.568 (15)	C(3)–C(4)	1.56 (2) 1.57
C(4)–C(5)	1.540 (14)	C(3)–C(9)	1.53 (2) 1.54
C(4)–C(7)	1.54 (2)	C(3)–C(10)	1.52 (2) 1.53
C(5)–C(6)	1.535 (15)	C(4)–C(5)	1.52 (2) 1.53
C(7)–C(8)	1.544 (15)	C(4)–C(7)	1.548 (15) 1.555
C(7)–C(9)	1.520 (14)	C(5)–C(6)	1.54 (2) 1.55
C(2)–C(1)–C(6)	104.8 (10)	C(2)–C(1)–C(6)	102.5 (9)
C(2)–C(1)–C(7)	97.6 (7)	C(2)–C(1)–C(7)	97.4 (9)
C(2)–C(1)–C(10)	116.4 (9)	C(2)–C(1)–C(8)	116.5 (10)
C(6)–C(1)–C(7)	100.1 (8)	C(6)–C(1)–C(7)	102.8 (10)
C(6)–C(1)–C(10)	115.0 (8)	C(6)–C(1)–C(8)	114.6 (11)
C(7)–C(1)–C(10)	120.1 (10)	C(7)–C(1)–C(8)	120.3 (10)
O–C(2)–C(1)	125.5 (11)	O–C(2)–C(1)	123.9 (12)
O–C(2)–C(3)	126.0 (11)	O–C(2)–C(3)	126.4 (12)
C(1)–C(2)–C(3)	108.5 (9)	C(1)–C(2)–C(3)	109.7 (10)
C(2)–C(3)–C(4)	101.3 (8)	C(2)–C(3)–C(4)	99.5 (9)
C(3)–C(4)–C(5)	105.8 (8)	C(2)–C(3)–C(9)	106.8 (10)
C(3)–C(4)–C(7)	101.9 (9)	C(2)–C(3)–C(10)	111.0 (10)
C(5)–C(4)–C(7)	102.7 (8)	C(4)–C(3)–C(9)	115.6 (10)
C(4)–C(5)–C(6)	102.5 (8)	C(4)–C(3)–C(10)	113.4 (11)
Br(1)–C(6)–C(1)	112.0 (7)	C(9)–C(3)–C(10)	109.9 (11)
Br(1)–C(6)–C(5)	112.4 (8)	C(3)–C(4)–C(5)	110.4 (9)
C(1)–C(6)–C(5)	106.4 (8)	C(3)–C(4)–C(7)	98.5 (9)
C(1)–C(7)–C(4)	95.3 (8)	C(5)–C(4)–C(7)	103.1 (9)
C(1)–C(7)–C(8)	112.7 (8)	C(4)–C(5)–C(6)	103.2 (9)
C(1)–C(7)–C(9)	111.3 (8)	C(1)–C(6)–C(5)	104.5 (9)
C(4)–C(7)–C(8)	115.1 (8)	Br(1)–C(7)–C(1)	112.8 (8)
C(4)–C(7)–C(9)	114.1 (9)	Br(1)–C(7)–C(4)	113.4 (9)
C(8)–C(7)–C(9)	108.1 (8)	C(1)–C(7)–C(4)	95.7 (8)
Br(2)–C(9)–C(7)	111.6 (7)	Br(2)–C(9)–C(3)	112.3 (8)

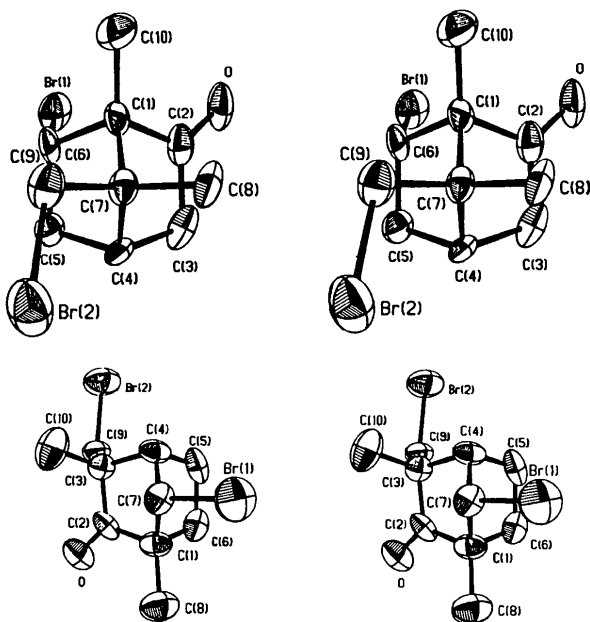


Fig. 1. Stereoviews of the dibromocamphor (top) and dibromofenchone (bottom) molecules. [In the latter, crystallographic numbering for the peripheral methyl groups is in the order of the numbers of the skeletal carbon atoms to which they are bonded; in the usual chemical numbering, C(8), C(9), C(10) are numbered 10, 9, 8, respectively. With respect to the 3-endo-9-dibromocamphor precursor, methyl groups in both products are scrambled as a result of the skeletal rearrangements (Money, 1985).]

925 reflections, $S = 2.41$ (refined enantiomorph, $wR = 0.057$, rejected at 99.5% significance level), 117 parameters [0.037, 0.041, 1.61 for 691 reflections (enantiomorph, $wR = 0.043$, rejected at 99.5% level), 119 parameters, including extinction correction, $g = 6.3(5) \times 10^4$], $R = 0.099$ for all 1336 reflections [0.087 for all 1207 reflections], $\Delta/\sigma = 0.09$ (mean), 0.36 (maximum) [0.03, 0.32], maximum final difference density -1.2 to $+1.8$ [-0.7 to $+0.4$] $e \text{ \AA}^{-3}$. Thermal parameters interpretable in terms of rigid-body motion for the fenchone derivative, bond lengths corrected for libration.

Discussion. Final positional parameters are in Table 1, and other data have been deposited.* The molecular structures (Fig. 1) are similar to those of other camphor derivatives (e.g. Rettig & Trotter, 1986). The analyses have established the absolute configurations (Fig. 1) for the (–)-enantiomorphs obtained from (+)-3-endo-9-

* Lists of anisotropic thermal parameters, H-atom positions, torsion angles and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43529 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure and Absolute Configuration of (1*R*,2*R*,4*R*)-2-[2-(4-Bromobenzoyloxy)ethyl]-1-methylbicyclo[2.1.1]hexan-5-one*

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Abstract. $C_{16}H_{17}BrO_3$, $M_r = 337.22$, orthorhombic, $P2_12_12_1$, $a = 7.253(1)$, $b = 7.949(2)$, $c = 26.520(2)$ \AA , $V = 1529.0(4)$ \AA^3 , $Z = 4$, $D_x = 1.464(1)$ g cm^{-3} , $Mo K\alpha$, $\lambda_{\alpha_1} = 0.70930$ \AA , $\mu = 27$ cm^{-1} , $F(000) = 688$, $T = 295$ K, $R = 0.047$ for 647 reflections. The bicyclohexane ring system contains a folded four-membered ring and two five-membered rings with envelope conformations. The bond distances in the ring system are slightly elongated, but otherwise molecular dimensions are close to expected values.

Introduction. The crystal structure analysis was undertaken to determine the structure and absolute configuration of an unusual rearrangement by-product

* IUPAC name: (1'*R*,2'*R*,4'*R*)-2-(1'-methyl-5'-oxo-2'-bicyclo[2.1.1]hexyl)ethyl 4-bromobenzoate.

dibromocamphor (Money, 1985; Antoniadis *et al.*, 1987). Bond distances and angles (Table 2) are close to normal values, with mean dimensions (identical in the two molecules): C–Br 1.97(1), C=O 1.21(1), C(sp^3)–C(sp^2) 1.52(1), C(sp^3)–C(sp^3) 1.54(1) \AA ; the C(1)–C(7)–C(4) bridgehead angles are 95.3(8) and 95.7(8)°. Intermolecular distances correspond to van der Waals interactions; shortest distances of each type in the two structures are: Br...Br 3.950(2), 3.719(2); Br...O 3.42(1), >4.5; Br...C 3.84(1), 3.81(1); C...C 3.81(2), 3.58(2); O...C 3.48(1), 3.28(1) \AA .

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formed in an enantiospecific synthesis from camphor of California red scale pheromone (Hutchinson & Money, 1986).

Experimental. Colourless needles along **b**, dimensions 0.14 × 0.75 × 0.18 mm, faces {010}, {001}, {101}, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with $\theta = 10$ –18°. Intensities for $\theta \leq 22^\circ$ (rapid fall off in intensity with angle, as a result of poor crystal quality; efforts to obtain better crystals were unsuccessful), hkl : 0 to 7, 0 to 8, 0 to 28, ω – θ scan, ω scan width (0.70 + 0.35tan θ)° at 0.75–6.7° min^{–1}, extended 25% on each side for background measurement, three standard reflections (no decay), Lp and absorption corrections, transmission factors 0.62–0.78, 1200 unique reflections measured, 647 with $I \geq \sigma(I)$, where $\sigma^2(I) =$