Bromine-initiated, Silicon-assisted Rearrangement in the Norbornene Series: Crystal and Molecular Structure of 3-*endo*,5-*endo*-Dibromotricyclo[2.2.1.$0^{2,6}$]heptane-7-carboxylic Acid †, ‡

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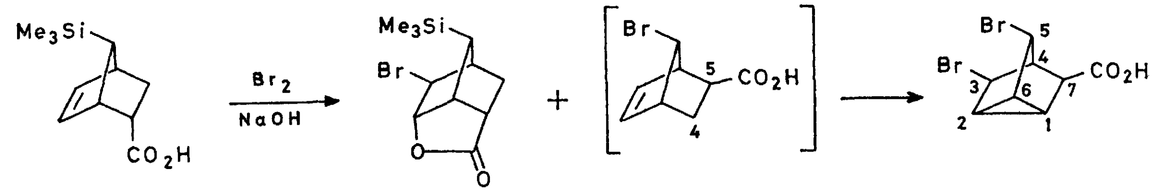
The structure (4) of the major product from the reaction of bromine on the sodium salt of 7-*anti*-trimethylsilylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid (1) has been elucidated by *X*-ray crystallography. The structure was solved by the heavy-atom method and refined by least-squares techniques to *R* 0.050 for 1 340 observed reflections measured by diffractometer. Crystals are monoclinic, space group $P2_1/n$, with $Z = 4$ in a unit cell of dimensions $a = 7.011(4)$, $b = 15.344(5)$, $c = 8.537(5)$ Å, $\beta = 99.97(4)°$.

THE reaction of bromine on the sodium salt of the silylated norbornene acid (1) gave a silicon-free dibromo-acid (4) (61%) in addition to the expected lactone (2). The structure of the unexpected dibromo-acid was revealed by the *X*-ray diffraction study reported in this paper. Evidently silicon-assisted rearrangement[1] has taken place in competition with lactonisation; the product of this rearrangement (3) has undergone further reaction of a precedented kind,[2] in which the main feature of interest is that the proton has been lost (presumably for stereoelectronic reasons) from C-4 rather than from C-5, even though the latter is α to the carbonyl group.



(1) (2) (3) (4)

EXPERIMENTAL

Syntheses.— 7-anti-*Trimethylsilylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylic acid* (1). Methyl 7-*anti*-trimethylsilylbicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylate[1] (357 mg, 1.58 mmol) was heated under reflux in a mixture of methanol (8 ml) and 2M aqueous sodium hydroxide solution (8 ml) for 1 h. The resulting solution was poured into 2M hydrochloric acid (25 ml) and this was extracted with chloroform (3 × 8 ml). The combined extracts were washed with brine, dried ($MgSO_4$), and solvent removed *in vacuo* to yield the *acid* (1) (311 mg, 94%), m.p. 69—72 °C. A sample, recrystallised from pentane at −15 °C, was obtained as needles, m.p. 75—76 °C (Found: C, 62.8; H, 8.6. $C_{11}H_{18}O_2Si$ requires C, 62.8; H, 8.65%); $\nu_{max.}$ ($CHCl_3$) 3 400—2 500 (CO_2H), 1 700 (C=O), 1 247, and 838 cm^{-1} ($SiMe_3$); δ($CDCl_3$) 10.5 (1 H, br s, CO_2H), 6.11 (1 H, dd, *J* 3 and 6 Hz, H_6), 5.89 (1 H, dd, *J* 3 and 6 Hz, H_5), 3.31 (1 H, m, H_1), 3.1—2.95 (2 H, m, H_2 and H_4), 1.94 (1 H, ddd, *J* 4, 9, and 12 Hz, $H_{3\text{-}exo}$), 1.46 (1 H, dd, *J* 4 and 12 Hz, $H_{3\text{-}endo}$), 0.96 (1 H, s, H_7), and −0.06 (9 H, s, $SiMe_3$); *m/e* 210 (2%, M^+), 195 (20, *M* − Me), 149 (15), 139 (20), 138 (100), 95 (33), and 73 (54).

Bromination of 7-anti-*trimethylsilylbicyclo*[2.2.1]*hept*-5-*ene*-2-endo-*carboxylic acid* (1). The acid (1) (346 mg, 1.65 mmol) was dissolved in methanol (8 ml) and 0.2M aqueous sodium hydroxide solution (8 ml) added such that the pH of the final solution was 8.0. Bromine (85 µl, 272 mg, 1.70 mmol) was added at room temperature and was immediately decolourised. After 0.5 h, the solution was made acidic (2M hydrochloric acid), diluted with water (50 ml), and extracted with dichloromethane (3 × 10 ml). The extracts were dried ($MgSO_4$), and solvent was removed *in vacuo*, to yield a crystalline mass (461 mg). This was dissolved in ether (25 ml) and extracted with saturated sodium hydrogen carbonate solution (3 × 10 ml). The organic phase, after being washed with brine, drying ($MgSO_4$) and evaporation of the ether *in vacuo*, yielded 5-exo-*bromo*-7-anti-*trimethylsilylbicyclo*[2.2.1]*heptane*-2,6-*carbolactone* (2) (147 mg, 31%), as needles, m.p. 120—121.5 °C [from acetone–light petroleum (b.p. 60—80 °C)] (Found: C, 45.4; H, 5.95. $C_{11}H_{17}BrO_2Si$ requires C, 45.7; H, 5.9%); R_F (benzene) 0.17; $\nu_{max.}$ ($CHCl_3$) 1 775 (C=O), 1 250 ($SiMe_3$), and 840 cm^{-1} ($SiMe_3$); δ(CCl_4) 4.89 (1 H, d, *J* 5 Hz, H_6), 3.78 (1 H, d, *J* 2 Hz, H_2), 3.25 (1 H, t with fine structure, *J* 5 Hz, H_1), 2.77 (1 H, br d, *J* 4 Hz, H_4), 2.50 [1 H, m (16 lines?), H_2], 2.09 (1 H, ddd, *J* 4, 10.5 and 13 Hz, $H_{3\text{-}exo}$), 1.85 (1 H, dd, *J* 2.5 and 13 Hz, $H_{3\text{-}endo}$), 1.14 (1 H, s with small further coupling, H_7), and 0.21 (9 H, s, $SiMe_3$); *m/e* 290 (1%, $^{81}M^+$), 288 (1%, $^{79}M^+$), 209 (16, *M* − Br), 139 (65), 137 (64), 119 (99), 108 (100), and 91 (96). The aqueous phase was made acidic with 2M hydrochloric acid and was extracted with dichloromethane (3 × 10 ml). The combined extracts were dried ($MgSO_4$), and solvent evaporated *in vacuo*, to yield 3-endo,5-endo-*dibromotricyclo*[2.2.1.$0^{2,6}$]*heptane*-7-*carboxylic acid* (4) (300 mg, 61%), m.p. 184—189 °C. This was recrystallised from ethyl acetate as needles, m.p. 188—190 °C (Found: C, 32.7; H, 2.85. $C_8H_8Br_2O_2$ requires C, 32.5; H, 2.7%); $\nu_{max.}$ ($CHCl_3$) 3 400—2 400 (CO_2), 1 706 (C=O), and 831 cm^{-1} (sharp); δ (deuterioacetone) 9.4—8.6 (br s, CO_2H), 4.36 and 4.31 (2 H, 2 × s, 2 × CHBr), 2.72 (2 H, s, H_4 and H_7?), 2.07 (2 H, d, *J* 5 Hz, H_2 and H_6?), and 1.70 (1 H, t with small further coupling, *J* 5 Hz, H_1); *m/e* 298, 296, and 294 (2, 4,

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† *Editor's note*. Strict application of I.U.P.A.C. nomenclature rules yields a different numbering system, *viz*. 5-*endo*,7-*endo*-dibromotricyclo[2.2.1.$0^{2,6}$]heptane-3-carboxylic acid.

‡ No reprints available.

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and 2%, M^+), 217 and 215 (50, 50, M − Br), 146 and 144 (17, 17), 137 (12), 136 (12), 135 (18), 118 (17), 107 (34), and 91 (100).

Single crystals of (4) were grown as colourless prisms by liquid diffusion of hexane into a chloroform solution.

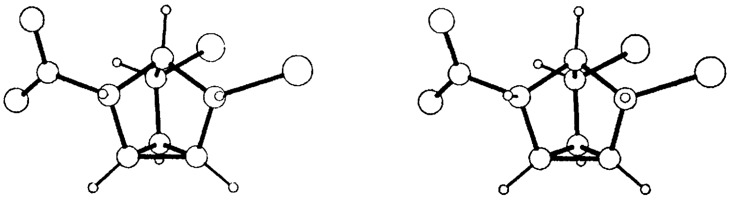

FIGURE 1 Stereoview of a single molecule of (4)

Crystal Data.—$C_8H_8Br_2O_2$, $M = 295.97$. Monoclinic, $a = 7.011(4)$, $b = 15.344(5)$, $c = 8.537(5)$ Å, $\beta = 99.97(4)°$, $U = 904.5$ Å^3, $D_c = 2.173$, $Z = 4$, D_m (flotation) $= 2.18$ g cm^{-3}. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) $= 87$ cm^{-1}. Space group $P2_1/n$ from systematic absences: $0k0$, k odd, and $h0l$, $h + l$ odd.

TABLE 1

Atom co-ordinates (× 10^4)

	x/a	y/b	z/c
Br(1)	7 322(1)	3 182(1)	6 673(1)
Br(2)	11 811(1)	2 429(1)	6 130(1)
O(1)	5 029(6)	162(3)	8 061(5)
O(2)	7 426(6)	296(3)	10 117(5)
C(3)	10 309(9)	1 386(4)	6 467(7)
C(5)	7 157(9)	1 920(4)	6 884(6)
C(8)	6 734(10)	308(4)	8 601(7)
C(2)	8 820(9)	1 119(4)	5 060(7)
C(4)	8 975(9)	1 459(4)	7 717(7)
C(1)	7 486(9)	510(4)	5 770(7)
C(7)	8 244(9)	498(4)	7 576(7)
C(6)	6 875(9)	1 431(4)	5 322(7)
H(31)	11 511	944	6 792
H(51)	5 965	1 896	7 532
H(21)	9 574	1 128	4 059
H(41)	9 598	1 742	8 849
H(11)	6 872	−130	5 511
H(71)	9 281	−8	7 988
H(61)	5 668	1 749	4 584

Overall isotropic temperature factor for H atoms: 0.047(7) Å^2.

TABLE 2

Bond lengths (Å)

C(3)–Br(2)	1.964(9)	C(3)–C(2)	1.505(10)
C(3)–C(4)	1.539(11)	C(5)–Br(1)	1.950(7)
C(5)–C(4)	1.521(10)	C(5)–C(6)	1.513(10)
C(8)–O(1)	1.225(8)	C(8)–O(2)	1.301(8)
C(8)–C(7)	1.514(12)	C(2)–C(1)	1.521(11)
C(2)–C(6)	1.498(11)	C(4)–C(7)	1.560(10)
C(1)–C(7)	1.541(10)	C(1)–C(6)	1.507(11)

TABLE 3

Bond angles (°)

Br(2)–C(3)–C(2)	114.9(5)	Br(2)–C(3)–C(4)	116.6(5)
C(2)–C(3)–C(4)	98.8(6)	Br(1)–C(5)–C(4)	116.5(5)
Br(1)–C(5)–C(6)	114.3(5)	C(4)–C(5)–C(6)	98.8(6)
O(1)–C(8)–O(2)	122.9(7)	O(1)–C(8)–C(7)	123.5(6)
O(2)–C(8)–C(7)	113.6(6)	C(3)–C(2)–C(1)	103.8(6)
C(3)–C(2)–C(6)	108.5(6)	C(1)–C(2)–C(6)	59.9(5)
C(3)–C(4)–C(5)	105.7(6)	C(3)–C(4)–C(7)	96.2(6)
C(5)–C(4)–C(7)	99.5(5)	C(2)–C(1)–C(7)	106.1(6)
C(2)–C(1)–C(6)	59.3(5)	C(7)–C(1)–C(6)	107.4(6)
C(8)–C(7)–C(4)	113.0(6)	C(8)–C(7)–C(1)	115.2(6)
C(4)–C(7)–C(1)	96.7(5)	C(5)–C(6)–C(2)	107.9(6)
C(5)–C(6)–C(1)	104.6(6)	C(2)–C(6)–C(1)	60.8(5)

2 294 reflexions in the range $0 < 2\theta < 55°$ were measured on a Syntex $P2_1$ diffractometer, by use of monochromated Mo-K_α radiation and a crystal 0.75 × 0.2 × 0.2 mm. After application of Lorentz polarization and empirical absorption corrections, averaging equivalent reflexions gave 1 340 unique reflexions with $F > 4\sigma(F)$. The structure was solved by conventional heavy-atom methods. In the final stages of refinement hydrogen atoms (identified from difference syntheses) were included with an overall isotropic temperature factor and with C–H fixed at 1.08 Å. The acidic hydrogen atom was not located. The final R' $[=\Sigma w^{\frac{1}{2}}\Delta/\Sigma w^{\frac{1}{2}}|F_o|]$ was 0.045, with a corresponding R of 0.050. The weighting scheme was $w = 1/[\sigma^2(F) + 0.0005F^2]$. Final atomic co-ordinates are given in Table 1, with derived interatomic distances and angles in Tables 2 and 3. Diagrams of the structure are given in Figures 1 and 2. The atom numbering system is indicated on structure (4). Observed and calculated structure factors, thermal parameters, and torsion angles are listed in Supplementary Publication No. SUP 22488 (11 pp., 1 microfiche).*

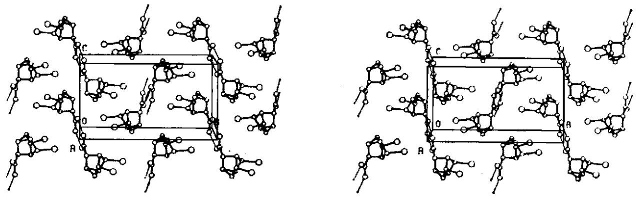

FIGURE 2 Stereo-packing diagram. Hydrogen bonds are indicated by narrow lines; hydrogen atoms omitted for clarity

The molecules are linked in dimers by typical carboxylic acid hydrogen-bonding, with O(2) ··· O(1) 2.61 Å [O(1) at $1 - x$, $-y$, $2 - z$] (Figure 2). Although the acidic hydrogen was not located, C–O bond lengths indicate that it is bonded to O(2).

We thank the M.R.C. for financial support and the S.R.C. for provision of the diffractometer. The Figures were drawn by use of the program PLUTO written by Dr. W. D. S. Motherwell; other crystallographic programs were written by Dr. G. M. Sheldrick.

[8/1586 *Received, 1st September,* 1978]

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1978, Index issue.

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